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A STUDY ON THE POSSIBLE USE OF CHAT
AND TAILINGS FROM THE OLD LEAD BELT OF
MISSOURI FOR AGRICULTURAL LIMESTONE

by

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and
Brian E. Davies

A STUDY ON THE POSSIBLE USE OF CHAT AND TAILINGS FROM THE OLD LEAD BELT OF MISSOURI FOR AGRICULTURAL LIMESTONE

A Research Report
Submitted to the
Missouri Department of
Natural Resources
P.O. Box 1368
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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

A STUDY ON THE POSSIBLE USE OF CHAT AND TAILINGS FROM THE OLD LEAD BELT OF MISSOURI FOR AGRICULTURAL LIMESTONE

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I. INTRODUCTION

Lead and zinc mining and milling procedures have historically produced large quantities of gange or waste rock from which most, but not all, of the ore minerals have been removed. From 1850 to 1960 three major lead and zinc mining districts were developed in Missouri's "Lead Belt" which contributed to the state becoming the primary producer of lead for the United States in 1902. Initially most of this production came from the "Old Lead Belt" in Madison and St. Francis Counties with St. Joseph Lead Company being the main producer. However, these resources became worked out and the mines in the Old Lead Belt were closed by 1965. This closure was also due to the discovery of the "Viburnum Trend" or "New Lead Belt" developed during 1968 which presently produces some 92% of the total U.S. lead production (1).

During the productive life of the "Old Lead Belt" two different methods of mineral beneficiation were employed. The first method used density separation of jigging which produced a coarse waste rock material called chat. This material was commonly disposed of in large piles or heaps often resembling small mountains. From 1915 to 1922, the froth flotation method of separating lead, zinc and copper from the parent rock by the use of chemical collectors was developed resulting in a finer particle waste rock material (tailings) and a more effective removal of sulphide minerals. Therefore, three general types of chat heaps or tailings piles exist in the "Old Lead Belt" area of Missouri. These are 1) chat; 2) tailings; 3) a mixture of chat and tailings representing historical changes in ore separation and mineral collection technology.

These rather dominant waste hills or deposits of chat or tailings, unless specially treated, will remain sterile of vegetation because of unfavorable physical properties (e.g., surface instability or moisture retention characteristics), lack of essential plant nutrients, and residual concentrations of heavy metals. The tailings or chat heaps may be unsightly and environmentally damaging if the rock waste material is blown or washed from the hills into neighboring fields or waterways (2). The most common ameliorative practice to date has been by landscaping and revegetation. However, the chat or tailings heaps also offer the possibility of being used as an economically valuable material such as in building foundations, highway construction and use of the calcareous material as agricultural limestone. However, questions were raised concerning residual heavy metal content which might restrict the use of tailings or chat for use as agricultural limestone purposes.

According to Davies and Roberts (3) and other studies (4), similar reuse of limestone tailings in north Wales (Great Britain) was believed to have contributed to the formation of a major contamination area (171 km^2 contaminated by Pb) resulting in significant problems of heavy metal uptake by vegetables. Also, the residual organic content following froth flotation had limited reuse in Derbyshire, England (5).

The Missouri Department of Natural Resources (DNR) has been constantly asked by the public and the mining industries if the tailings, or chat, materials in the Old Lead Belt area might be used as agricultural limestone thereby presenting a potential for resource reuse and contributing to removal of a possible pollution source. However, additional research information was needed on the chemical characterization and metals possibly available to soil and plants if the tailings or chat materials were to be used for agricultural lime purposes.

Based on the needs of the Missouri DNR, a research study was designed and performed to answer these important research questions.

II. OBJECTIVES

Based on the needs noted and a request from the Missouri DNR, the objectives of this study were to:

1. Characterize physical and chemical composition of selected chat and tailings piles in the "Old Lead Belt" and "New Lead Belt."
2. Collect and analyze soil and vegetation samples from fields where tailings or chat have been previously used as agricultural lime.
3. Collect and analyze soil and vegetation samples from control areas where commercial limestone has been applied for at least five years.
4. Perform bioassays for plant uptake of metals in radish and lettuce plants grown on uncontaminated soil, agricultural limestone (controls) and soils treated with tailings or chat with the pH adjusted to 7 or neutral.
5. Summarize and evaluate analytical results to determine if selective tailings or chat materials might be used for agricultural purposes without the bioconcentration of heavy metals from the soil to the plant system at levels which might be of concern to public health.

III. RESEARCH METHODOLOGY

A research program was proposed which involved both survey, experiemntal and analytical work with the objectives of characterizing the Old Lead Belt chat and tailings chemically and establishing, if these materials were applied to the land as agricultural limestone, whether they might release heavy metals to the soil-plant system at levels of concern for public health. Since the Old Lead Belt initially utilized older, less efficient extractive technologies, it was proposed to also survey some selected tailings from newer mining operations in the Viburnum Trend where more effective ore concentration techniques are presently employed.

In St. Francois County there are six major chat or tailings areas: at Leadwood, down the Big River to the Desloge pile in a meander loop of the river; at Bonne Terre; the Elvins tailings pile; the Federal tailings pile; and the National tailings pile at Flat River, Missouri. All except the Federal tailings were studied in the Old Lead Belt. Two further tailings piles were investigated in the New Lead Belt at the St. Joe Viburnum operation and the Cominco American Magmont Mine.

Meetings were held with the Missouri DNR project director, Mr. John C. Ford, and a statistical package was developed for the necessary number of samples needed for each chat or tailings pile to attain the level of confidence needed by the Missouri DNR. The number of samples collected followed the population standard deviation suggested for the 95% confidence level.

A. Tailings and Chat

Tailings and chat samples were taken along a number of transects which were determined to be most representative of the tailings or chat pile. At each sample location, samples were collected from approximately the 20 - 40 cm depth below the surface. This was intended to distinguish between weathered and leached surface material and the less altered interior material. Samples were bagged in polyethylene and labelled as to location in the respective pile. The material was returned to the laboratory, air dried, and sieved with the less than 40-mesh fine fraction being dissolved in nitric acid and analyzed for lead, cadmium and zinc by atomic absorption (AAS) or the inductively coupled argon plasma (ICAP) method.

B. Soils

Two fields were located where tailings had been applied for lime supplementation for at least the past five years. The pedological nature of the soil were established at each site with the assistance of Mr. Burton L. Brown of the Soil Conversation Service, and at each site a random survey of the topsoil was made using the standard 'staggered W' method. Samples were comprised of auger cores to a depth of 10 cm which were then bulked in a polyethlene bag.

Soils were then returned to the laboratory where they were dried at room temperature, gently ground and passed through a 2 mm nylon sieve. Metal ananysis was performed by the Environmental Trace Substances Research Center in Columbia, Missouri using the AAS (flame or graphite furnace or ICAP method.

C. Vegetation

The plant material was cropped with stainless steel implements and placed in a polyethylene bag and then, in turn, in a second bag with the sample label. Label and sample record sheet contained the same information as used for soil samples. As soon as practicable, the samples were placed in an ice chest.

In the laboratory the plant material was carefully washed by accepted methods and dried at 100°C followed by milling. Analysis (wet or dry ashing) was made by AAS or ICAP as previously described.

D. Bioassays

Radish and lettuce were the two experimental plants used for controlled growth experiments.

Pots used in the study were 20 cm/8 in commercial plastic. Soils were brought in to the laboratory, spread thin on plastic sheeting and large debris removed. The soils were sampled for analysis and then potted and mixed with 25% volume of inert (e.g., chert) grit. After the soils were analyzed each pot was emptied on to the plastic and the appropriate amount of lime and fertilizer mixed in. The soils were then returned to the pot, watered with deionised water and allowed to stand for 48 hours to equilibrate. Each pot was then sown with 25 seeds of the respective plant and the seeds allowed to germinate and grow. They were then thinned to 5 plants per pot and allowed to grow to maturity. After plant harvest, the pot soils were reanalysed.

Soils were derived from localities identified during the earlier survey work with a sufficient amount excavated to fill the pots. Soils were returned to the laboratory in plastic sacks contained within plastic trash cans.

All pot treatments were triplicated and received a basal treatment of NPK compounded from laboratory pure chemicals. The soils used comprised an uncontaminated control soil, the same with sufficient agricultural limestone to adjust the pH to approximately 7, a soil known to have been treated with dolomitic tailings, the control soil plus metal-rich tailings from the Old Lead Belt sufficient to raise pH to approximately 7, the control plus tailings from the New Lead Belt sufficient to raise pH to approximately 7.

When the plants were harvested, the yield from each plot was weighed immediately after the soil was washed from the roots with deionised water. Lettuce was divided into leaves and roots, the leaves weighed and root length measured. Radish was divided into leaves, bulb and roots, leaves and bulbs weighed, and analyzed for Pb or Cd.

E. Commercial Limestone

Thirteen samples of commercial agricultural limestone were obtained and submitted to the Environmental Trace Substances Research Center in Columbia, Missouri for ICAP analyses. These samples represented four out-of-state samples and nine samples representative of the different locations within the State of Missouri that are presently producing agricultural limestone.

F. Quality Control

Since this study needed to determine if selected chat or tailings may be used for agricultural lime purposes, an efficient quality control method was necessary. In order to maintain this sixteen (16%) of the study samples were analyzed by the Environmental Trace Substances Research Center (ETSRC) in Columbia, Missouri. Also, selected sample duplicates and spikes were incorporated into the analytical program at the University of Missouri-Rolla (UMR) and the ETSRC to validate analytical results.

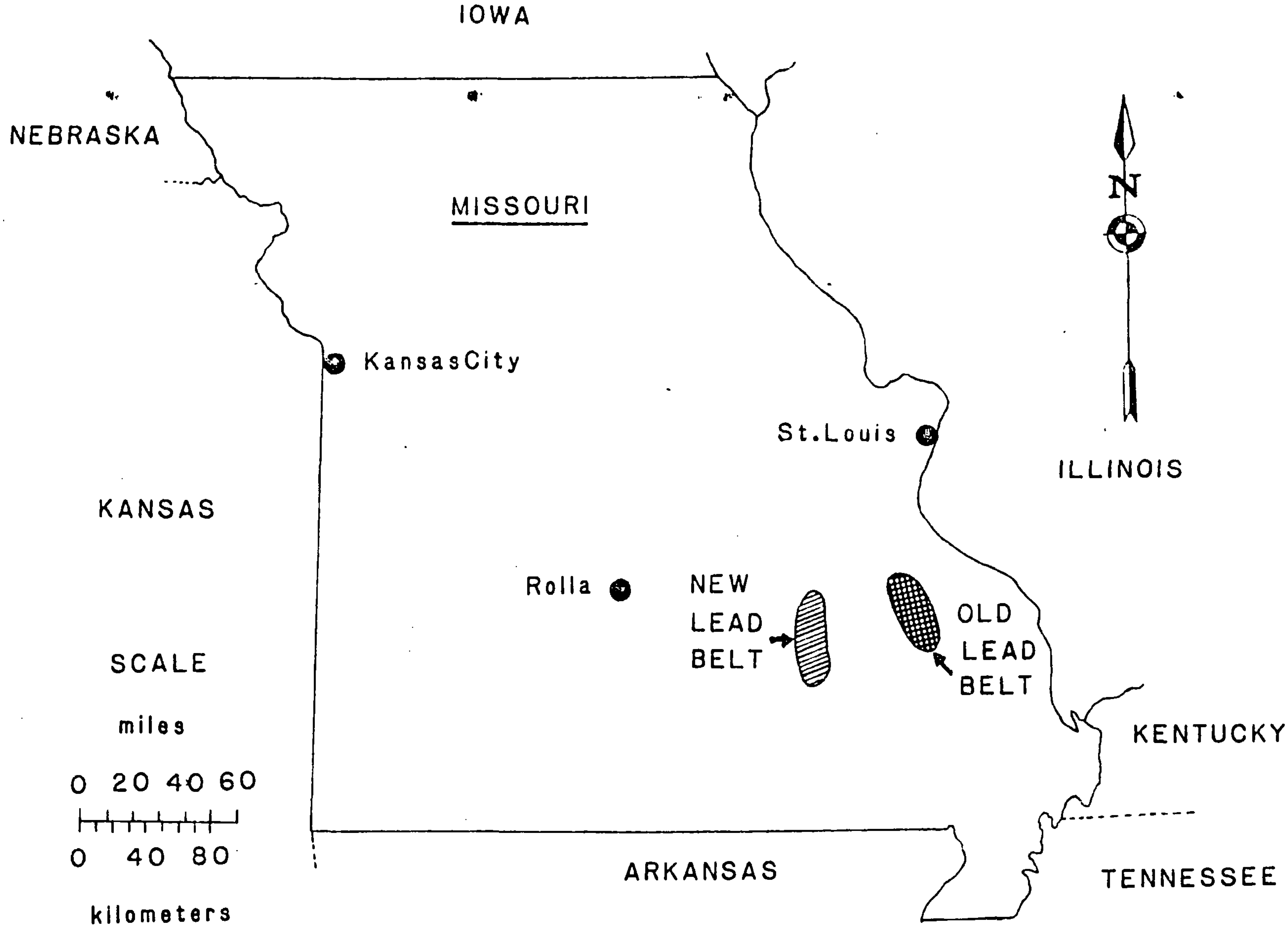
IV. STUDY AREA

The study area selected for this investigation is comprised of the Leadwood, Big River, Desloge, Elvins, National and Bonne Terre tailings piles within the confines of the Old Lead Belt in St. Francois County, Missouri. The Old Lead Belt is located about 113 km (70 mi) south of St. Louis, Missouri and contains the cities of Bonneterre, Leadwood, Elvins, Desloge, and Flat River. This old mining region covers an area of approximately 285 sq km (110 sq mi) and is bordered by latitudes $38^{o}00'$ and $37^{o}49'5''$ and by longitudes $90^{o}37'30''$ and $90^{o}28'45''$.

According to a report submitted by Heyward M. Wharton to the St. Joe Minerals Corporation on 28 October 1983 (6) the acreage affected by inactive lead-zinc mining in the "Old Lead Belt" represented 3085 acres as contrasted with the 1822 presently impacted by active or development mining operations in the "Viburnum Trend." Figure 1 provides a visual perspective of the area including its location with respect to major cities in Missouri.

The topography consists of gently rolling hills with narrow table-lands areas and alluvial plains comprise most of the topography in the Old Lead Belt, with the exception of the extreme southwestern portions of St. Francois County, which is mountainous (7). Hickory, elm, and sycamore trees compliment the lowland stream areas, while red, white and black oaks are abundant in the upland areas (8).

The climate of this region usually consists of warm, humid summers, and mild winters. Extremes of $-30^{o}F$ ($-34^{o}C$) and $115^{o}F$ ($46^{o}C$) have been



LOCATION OF OLD AND NEW LEAD BELTS OF MISSOURI

FIGURE 1

recorded, but are not common to the area. Annual rainfall averages generally total about 40 inches (9).

Galena, the most important mineral ore of lead, was the principle ore mined within the Old Lead Belt of Missouri (10,11). Normal thickness of this mineralization varied from a few inches to about 6.1 m (20 ft.). These ore deposits were horizontal, concentrated along flat shale bands or other easily permeated plains, and found in the Bonne Terre dolemite with thicknesses of nearly 131 m (400 ft). The La Motte sandstone, with thicknesses up to 400 feet, underlies this dolemite, while shale and siliceous dolemite, in thicknesses up to 152 m (500 ft) is found above it.

V. CHARACTERIZATION OF TAILINGS AND CHAT PILES

Five different tailings or chat piles within the Old Lead Belt area were selected for sampling. These were the Leadwood, Big River-Desloge, National, Elvins and Bonne Terre (two areas) tailings piles illustrated in Figure 2.

These tailings and chat piles in the Big River area of the "Old Lead Belt" were subjected to metal sampling to determine the amounts of lead, cadmium and zinc present. Since some of the chat piles which were generated before the introduction of the froth flotation extraction technology, around 1917, contain larger gangue particles and more metals, it was necessary to categorize these tailings or chat disposal areas which are a contributing source for tailings material (and metals) introduced into the sediments of Big River through storm water runoff.

Concentrations of lead in sediments and water of the Big River are shown in Figures 3 and 4. These sediment data indicate that the highest concentrations of lead were found near the confluence of Eaton Creek with the Big River at Leadwood. Lead concentrations of the sediments derived from the Desloge tailings pile are uniformly in the range of 1,000-3,000 ppm and the sediment data reflect the composition of this tailings pile (12). Concentrations of lead in river water are quite low throughout the region, including water from over river sediments shown to have anomalously high lead concentrations (5 ppb lead in water at Leadwood). In most instances, the lead concentrations remain below the recommended limits for drinking water standards. This is consistent with the known limited solubility of lead compounds in hard, alkaline

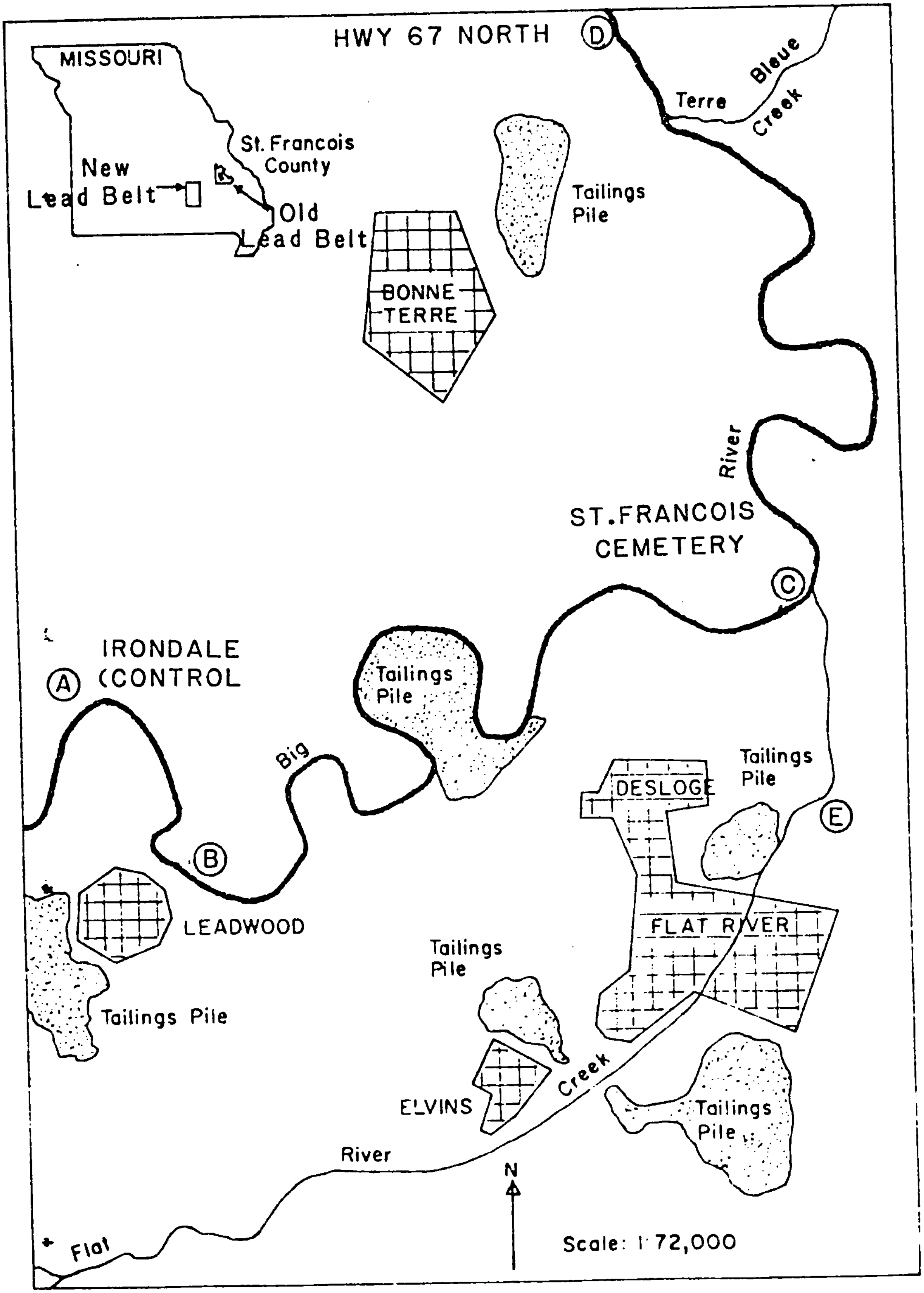


FIGURE 2. LOCATION OF TAILINGS PILES STUDIED IN THE OLD LEAD BELT.

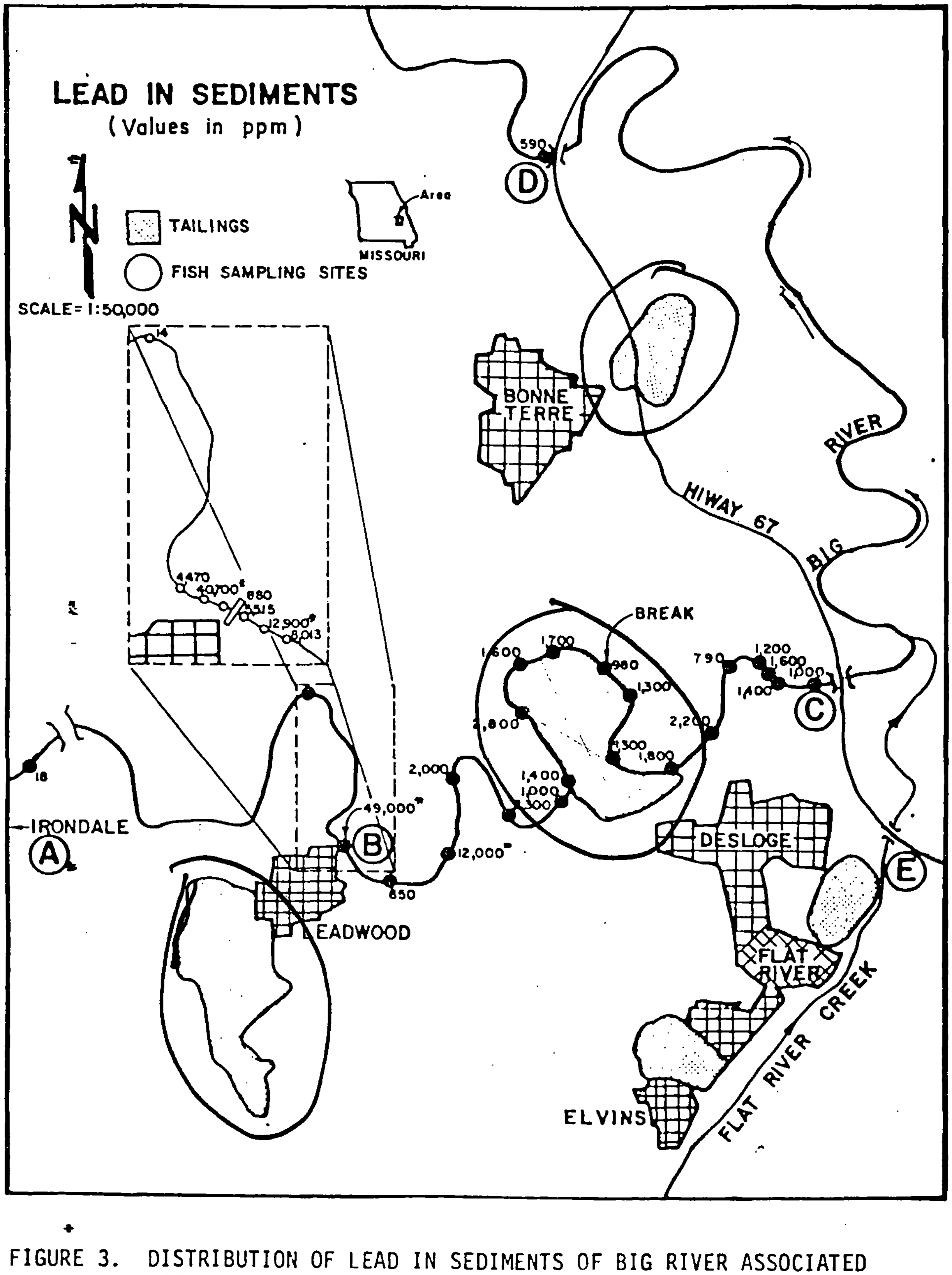


FIGURE 3. DISTRIBUTION OF LEAD IN SEDIMENTS OF BIG RIVER ASSOCIATED WITH TAILINGS PILES.

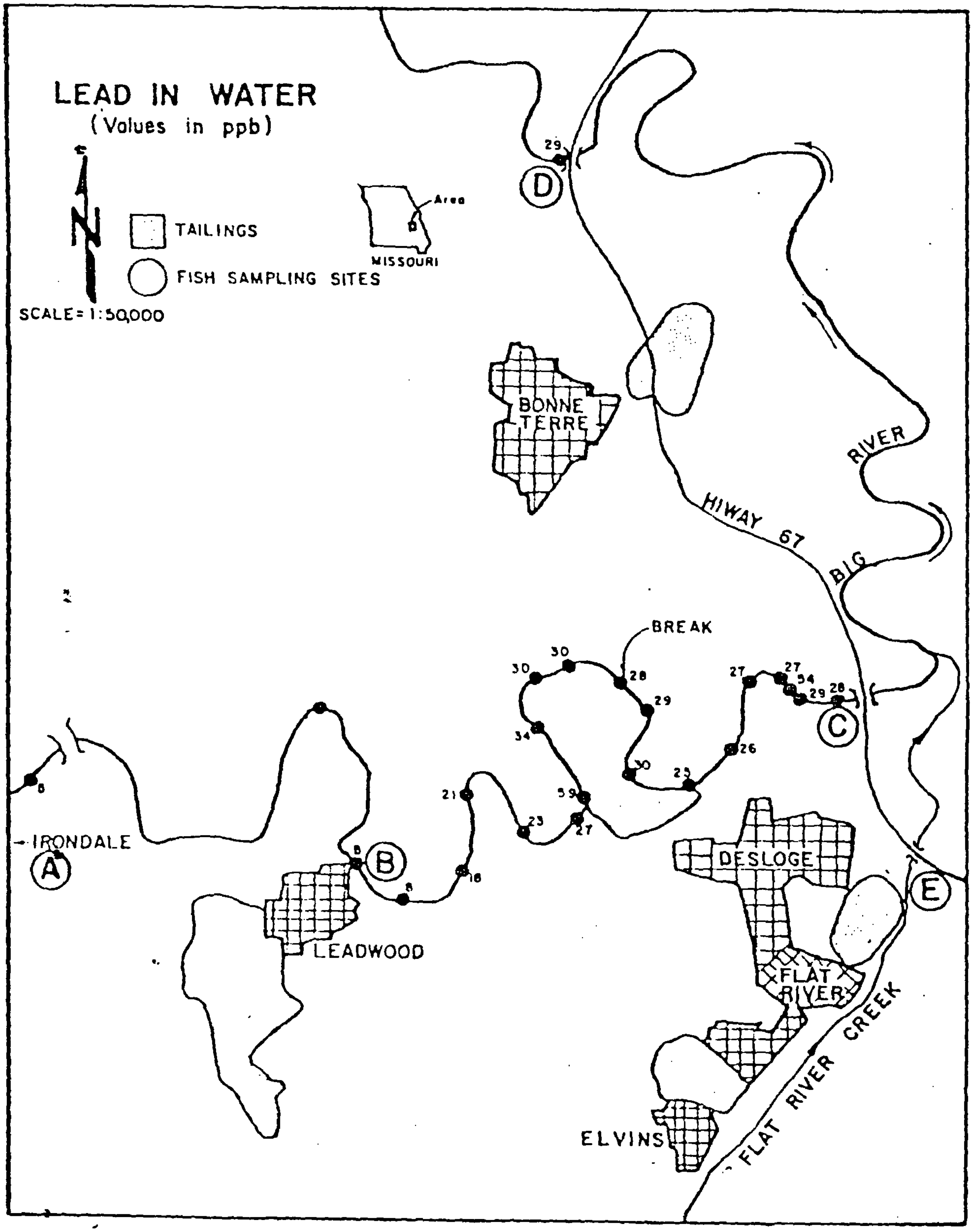


FIGURE 4. LEAD IN WATER OF BIG RIVER IN THE OLD LEAD BELT REGION OF MISS URI.

waters. The two notable exceptions were: 1) a sample of water taken directly from a pipe from an old drill hole (59 ppb) some distance upstream of the eroded break in the Desloge tailings pile, and b) a sample taken from the Big River at the junction with sewage effluent from the Desloge-Flat River city sewage treatment plant (54 ppb).

Sampling transects were designed to take the most representative samples of tailings (or chat) material from the unweathered portion (depth of 20 cm) of the piles in sufficient numbers to meet the Missouri DNR statistical program discussed in the methods section of the report and included in the Appendix. Sampling locations were noted by number on the appropriate tailings figures and followed by tables giving the metal values for Pb, Cd, and Zn.

The National tailings pile was the subject of a M.S. thesis by Elliott (15) and only the pertinent findings are discussed in this report. However, a copy of Elliott's thesis (15) will accompany the report as a part of the research evaluation.

Individual tailings or chat piles are discussed according to characterization by sampling data. A statistical analysis and evaluation of the different tailings piles is included at the end of this section of the report.

A. Leadwood

A series of transects were established for the Leadwood tailings and chat pile located along the eastern border of the town of Leadwood, Missouri and extending slightly to the south of town. Figure 5 illustrates the samples numbering for the 98 samples taken at near-surface unweathered

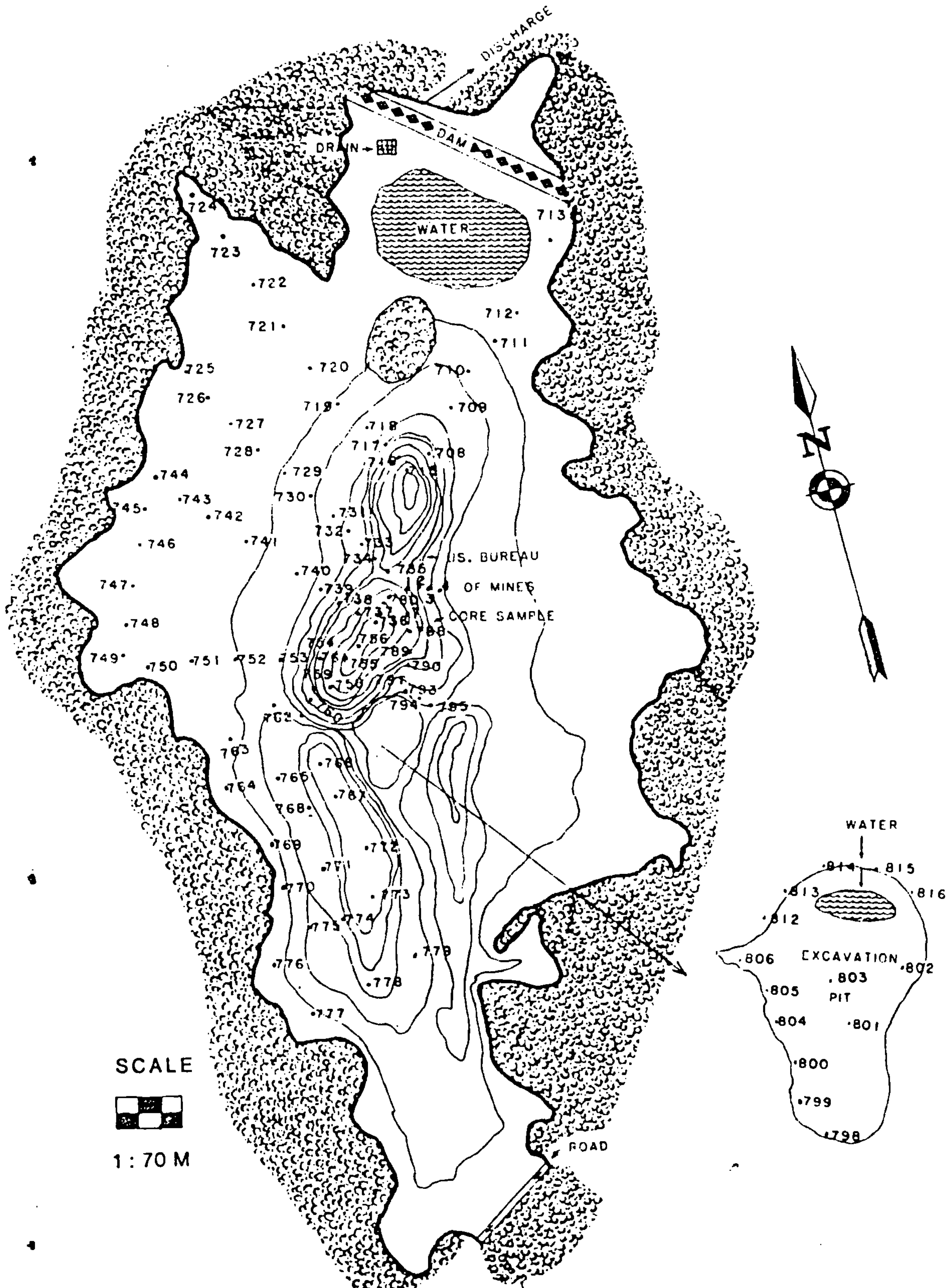


FIGURE 5. LOCATION OF SAMPLING SITES ON LEADWOOD TAILINGS PILE

materials. Table I indicates the metal concentrations for Pb, Cd, and Zn in micrograms per gram (parts per million) by sample number.

Since the U.S. Department of the Interior Bureau of Mines was performing a research study associated with tailings deposits in the "Old Lead Belt", a cooperative effort was worked out with their research people whereby the near surface sampling results would be shared with them in return for the Bureau of Mines coring down to the bottom of the Leadwood and National tailings piles. Mr. Larry George, Glynn Horter and Scot Lay assisted with the coring procedure and Figure 6 illustrates the location of the hand augered samples (two-to-four foot depth) and the drill hole locations which extended to twelve feet at one location and twenty four feet at a second location to reach bedrock under the Leadwood tailings pile. Table 2 gives the Pb, Cd, and Zn concentrations associated with the hand augered samples and the two coring drill holes. (Courtesy of the Bureau of Mines). Table 3 gives the inductive coupled argon plasma (ICAP) analysis for the core samples at site R-1 down to 24 ft. and Table 4 gives the ICAP data for the core samples at site R-2 down to 12 ft or bedrock.

The highest lead values found for the Leadwood tailings pile were 17,000 micrograms per gram which came from a site close to the earthen dam at the north-eastern portion of the area. The next highest sample of 13,800 ppm came from the center of the excavated pit on the south side of the main pile. Shallow hand augered samples did not show a significant change in composition down to a depth of four feet.

TABLE - 1
LEADWOOD TAILINGS PILE

Sample No.	Metal Conc; ug/g Pb	Cd	Zn
L708	1320	66.9	3490
L709	1880	89.7	4750
L710	1630	63.6	3550
L711	1110	40.0	2290
L712	2420	67.4	3570
L713	17000	158	8630
L714	9500	243	15200
L715	1620	88.8	4150
L716	1800		4940
L717	2310	105	5150
L718	1900	87.5	4370
L719	1780	66.0	3100
L720	2580	74.5	3630
L721	1830	49.5	1710
L722	1680	47.5	2180
L723	1510	39.6	1980
L724	2280	41.6	1880
L725	1620	37.6	1600
L726	1020	42.3	1830
L727	2580	70.6	3250
L728	1620	57.2	2860
L729	3310	115	6040
L730	1020	64.0	3200
L731	1990	111	6150
L732	1860	101	5620
L733	1630	101	5340
L734	1260	171	9720
L736	2530	98.9	4650
L737	1600	96.7	4830
L738	1630	94.2	4510
L739	1720	78.3	3720
L740	919	44.0	1600
L741	886	28.3	1040
L742	761	30.4	1050
L743	823	34.5	1340
L744	986	33.5	1300
L745	2170	83.7	7980
L746	832	75.3	3760
L747	1430	763	3820
L748	1070	596	2880
L749	890	763	3560
L750	880	547	2930
L751	2520	1610	8530
L752	2300	1870	10100
L754	2260	1720	8320

(CONTINUED)
TABLE - 1
LEADWOOD TAILINGS PILE

Sample No.	Metal Conc; ug/g Pb	Cd	Zn
L755	1170	1230	6060
L756	1900	1350	7060
L758	1950	995	5460
L759	4740	1120	5890
L760	920	45.9	2480
L761	1050	625	3520
L762	1880	858	4390
L763	1430	1200	6730
L764	1670	856	4480
L765	736	1010	5570
L766	3420	20.4	1710
L767	597	308	1250
L768	3290	20.3	1430
L769	1330	372	1660
L770	1400	721	3420
L771	1300	15.9	987
L772	2260	77.2	4050
L773	788	31.1	1280
L774	1120	44.3	2210
L775	916	46.7	2240
L776	2600	37.9	1710
L777	909	85.0	4250
L778	1140	56.3	3010
L779	1130	55.6	2780
L780	3640	155	8610
L781	2550	249	14600
L782	7470	220	13600
L783	4320	162	9180
L784	3490	151	8460
L786	1120	37.3	1960
L787	1250	67.2	3660
L788	934	46.9	2530
L789	615	9.3	633
L790	1640	77.3	4050
L791	3770	78.4	4220
L792	5560	78.7	5214
L793	1270	70.2	3980
L794	1100	84.6	4720
L795	10100	456	25800
L798	1380	47.2	2460
L799	1360	46.7	2630
L800	1710	80.5	4790
L801	1970	76.4	3910
L802	8230	278	15800
L803	13800	524	
L804	1440	69.2	3930

(Continued)
TABLE - 1
LEADWOOD TAILINGS PILE

Sample No.	Metal Conc; ug/g Pb	Cd	Zn
L805	1740	69.6	3970
L806	2830	87.8	5380
L812	6200	177	9900
L813	4180	325	19600
L814	3521	147	8320
L815	4340	158	9570
L816	2490	137	8850

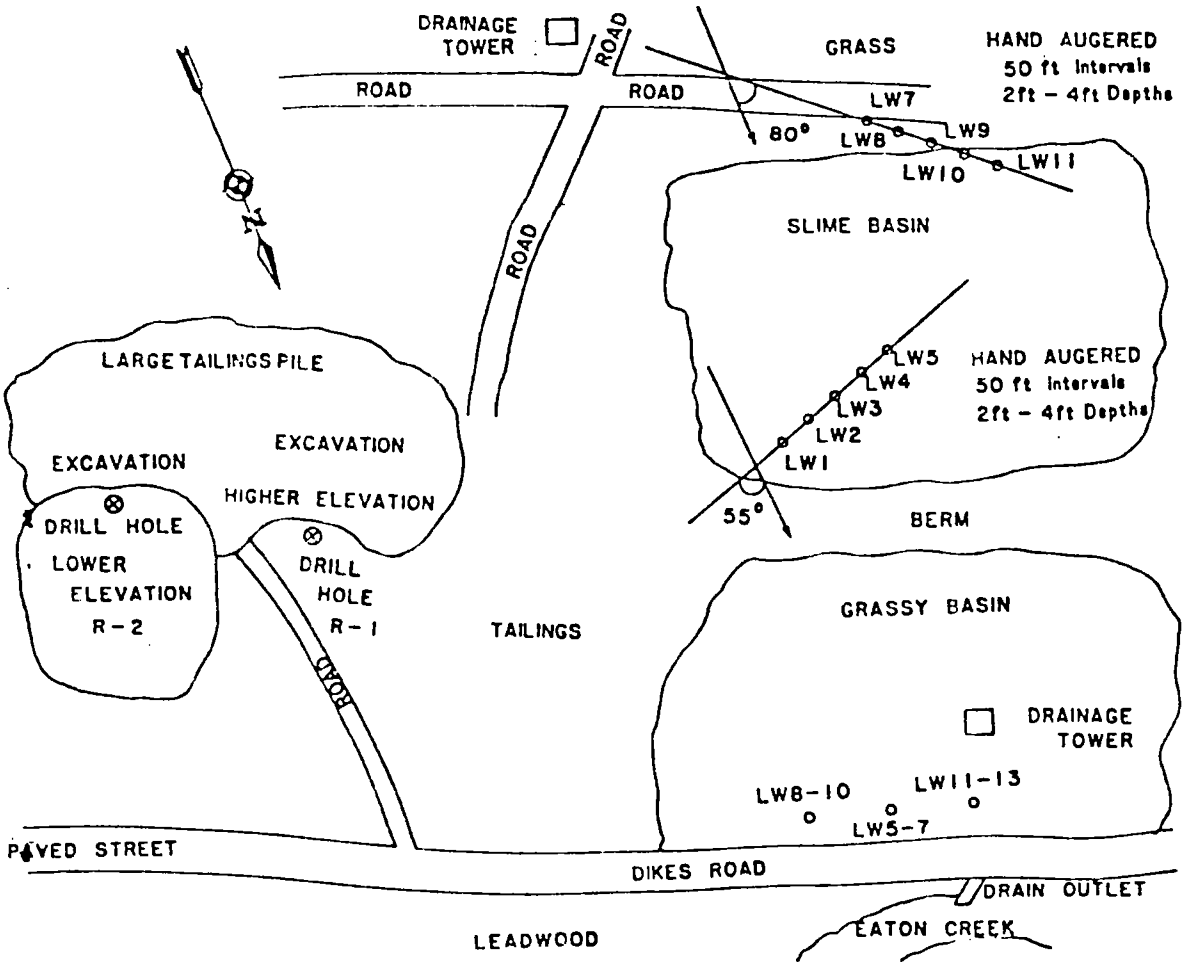


FIGURE 6. LOCATION OF U.S. BUREAU OF MINES AUGER AND CORE SAMPLING SITES ON LEADWOOD TAILINGS PILE.

TABLE 2
AUGER AND CORE SAMPLING OF
LEADWOOD TAILINGS PILE (Courtesy Bureau of Mines)

Sample No.	Metal Conc; ug/g		
	Pb	Cd	Zn
Surface			
LW 5-7	2200	40	833
LW 8-10	2167	37	800
LW 11-13	2850	35	500
Augered - Surface - two - four foot depth			
LW 1-Surface	1300	40	1000
LW 1-2 ft	600	40	400
LW 1-4 ft	700	30	300
LW 2-Surface	1600	40	1200
LW 2-2 ft	2000	40	1100
LW 2-4 ft	2500	40	1300
LW 3-Surface	600	30	400
LW 3-2 ft	1200	40	1000
LW 3-4 ft	700	30	800
LW 4-Surface	1600	80	1300
LW 4-2 ft	3200	80	1300
LW 4-4 ft	4000	100	1800
LW 5-Surface	2000	130	1800
LW 5-2 ft	2400	100	1700
LW 5-4 ft	2800	110	1400
LW 7-Surface	1400	110	1000
LW 7-2 ft	1200	90	1300
LW 7-4 ft	1500	70	1400
LW 8-Surface	1400	50	1000
LW 8-2 ft	1500	80	1100
LW 8-4 ft	1600	80	1200
LW 9-Surface	1500	90	1200
LW 9-2 ft	1500	100	1000
LW 9-4 ft	1500	120	1300
LW 10-Surface	1300	40	1000
LW 10-2 ft	1000	40	1000
LW 10-4 ft	1900	60	1600
LW 11-Surface	2600	50	1200
LW 11-2 ft	1100	60	1700
LW 11-4 ft	1000	60	1400

TABLE 2 (Cont.)
AUGER AND CORE SAMPLING OF
LEADWOOD TAILINGS PILE (Courtesy Bureau of Mines)

Sample No.	Metal Conc; ug/g		
	Pb	Cd	Zn
Rotary Cored	Pb	Depth.	
R-1	5000	3 ft	
	5100	6	
	5500	9	
	5200	12	
	4900	15	
	4500	18	
	4300	21	
	4600	24 - Bottom on tailings	
R-2	16600	3 ft	
	12100	6	
	10400	9	
	10500	12 - Bottom of tailings	

TABLE 3
ROTARY CORE SAMPLING OF LEADWOOD TAILINGS DEPOSIT
INDUCTIVE COUPLED ARGON PLASMA ANALYSIS (ICAP) FOR SITE R-1 BY DEPTH
(UNITS ARE MICROGRAMS/GRAM)

Element	3 ft	6 ft	9 ft	12 ft	15 ft	18 ft	21 ft	24 ft
Ag	20.	20.	17.	21.	15.	8.	9.	10.
Al	830.	820.	1200.	720.	520.	490.	760.	740.
As	9	9.	9.	7.	5.	5.	6.	6.
B	5.	6.	10.	6.	6.	5.	5.	3.
Ba	11.	3.4	7.0	6.7	4.9	3.6	4.0	3.4
Be	0.89	1.0	1.1	0.96	0.83	0.83	1.0	0.9
Ca	190,000.	190,000.	180,000.	180,000.	190,000.	190,000.	190,000.	190,000.
Cd	250.	270.	180.	170.	160.	130.	120.	120.
Co	27.	32.	37.	37.	35.	32.	33.	30.
Cr	6.8	4.3	10.	18.	20.	22.	25.	41.
Cu	15.	12.	12.	14.	15.	11.	13.	10.
Fe	19,000.	19,000.	20,000.	20,000.	20,000.	21,000.	21,000.	20,000.
Li	2.	1.	2.	1.	1.	1.	1.	2.
Mg	100,000	100,000.	99,000.	100,000.	100,000.	100,000.	100,000.	100,000.
Mn	3400.	3400.	3400.	3500.	3500.	3600.	3600.	3500.
Mo	20.	20.	20.	30.	30.	30.	30.	20.
Ni	16.	18.	18.	23.	18.	18.	23.	16.
P	190.	200.	210.	210.	210.	200.	190.	190.
Sb	9.	8.	9.	9.	10.	10.	9.	9.
Se	10.	10.	20.	40.	30.	30.	30.	20.
Si	180.	340.	160.	250.	210.	140.	100.	110.
Sn	<2.	<2.	<2.	<2.	<2.	<2.	<2.	<2.
Sr	50.	52.	50.	50.	50.	51.	50.	51.
Ti	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
V	4.	4.	4.	4.	4.	4.	4.	3.
Zn	13,000	14,000.	9800.	9800.	8400.	7300.	6600.	6300.

TABLE 4
ROTARY CORE SAMPLING OF LEADWOOD TAILINGS DEPOSIT
INDUCTIVE COUPLED ARGON PLASMA (ICAP) ANALYSIS FOR SITE R-2 BY DEPTH
(UNITS ARE MICROGRAMS/GRAM)

Element	3 ft	6 ft	9 ft	12 ft
Ag	23	30.	27.	24.
Al	1800.	1000.	1100.	760.
As	10.	10.	10.	10.
B	10.	8.	3.	<2.
Ba	7.3	6.0	7.3	8.1
Be	1.1	1.0	1.0	0.66
Ca	160,000.	170,000.	170,000.	150,000.
Cd	350.	450.	430.	420.
Co	53.	74.	86.	130.
Cr	6.8	11.	16.	54.
Cu	15.	15.	17.	22.
Fe	20,000.	20,000.	21,000.	21,000.
Li	3.	2.	2.	1.
Mg	90,000.	90,000.	90,000.	82,000.
Mn	3200.	3200.	3300.	3000.
Mo	20.	30.	30.	30.
Ni	25.	37.	50.	67.
P	240.	230.	240.	270.
Sb	9.	7.	4.	<3.
Se	10.	20.	10.	10.
Si	96.	470.	130.	220.
Sn	<2.	<2.	<2.	<2.
Sr	46.	45.	45.	41.
Ti	<0.3	<0.3	<0.3	<0.3
V	6.	5.	5.	4.
Zn	19,000.	23,000.	23,000.	23,000.

The rotary core samples were taken in the area where prior sampling had indicated that the chat contained elevated levels of metals and probably represented the oldest part of the deposit. The R-1 site was cored to the bedrock at the bottom of the pile which represented a depth of 24 feet. Samples were taken every three feet and analyzed for a complete host of elements by the ICAP method. Lead at this location did not show an increase toward the bottom of the hole but remained in the 4600 to 5000 ppm range. The water brought up in the coring samples was fresh and without any anaerobic smell which leads one to postulate that the rainwater leachate is moving away from the tailings pile to the drain at the northern edge of the tailings area. ICAP data also indicates that the concentration of other elements tends to remain fairly constant again indicating a more rapid flow through of rainwater with no appreciable concentrations at the bottom of the chat deposits.

The rotary core samples at site R-2 were started in a depression some 12 feet lower than the R-1 site and approximately 100 yards to the south of the R-1 site. Lead concentrations at the surface ran 16,600 ppm and decreased to 10,500 ppm at the 12 foot depth or bottom of the hole at dolomite bedrock. Again the water brought up with the samples did not contain any anaerobic odor and was of a quality that could be attributed to rainfall. The ICAP data for the R-2 site did not exhibit any unusual increases or decreases in the elements surveyed which seemed to further confirm the rapid penetration and subsurface flow of storm runoff water through the tailings pile and into the drain for Eaton Creek branch.

B. Big River-Desloge

The Big River-Desloge tailings pile is located on a turn of the Big River approximately two miles downstream from Leadwood, Missouri and east of the town of Desloge, Missouri. During the past four years, this tailings pile received much attention from the regulatory agencies, researchers and the press due to a break in the elevated pile allowing for the discharge of tailings into the Big River along the eastern slope.

The Kansas City Times headline article of March 28, 1981 carried a banner headline saying "Old Mines Leave a Legacy of Danger" (13) which expressed concern about repairs to hald the runoff of lead.

The break has since been repaired but the unstability of the tailings pile along the eastern slope and bordering the Big River remains to be a problem.

Figure 7 illustrates the sampling pattern employed in characterizing the Big River-Desloge tailings pile. Table 5 gives a listing for Pb, Cd and Zn concentrations found for the various sample sites. A total of 74 samples were taken to meet the statistical requirements suggested by the Missouri Department of Natural Resources (14).

C. National

The National tailings pile is situated in the northern portion of Flat River, Missouri and is shaped like a large dome covering approximately 1.3 square km (0.5 square miles) in area. Storm water runoff from the tailings area is discharged into Flat River creek which flows some three miles before it discharges into the Big River.

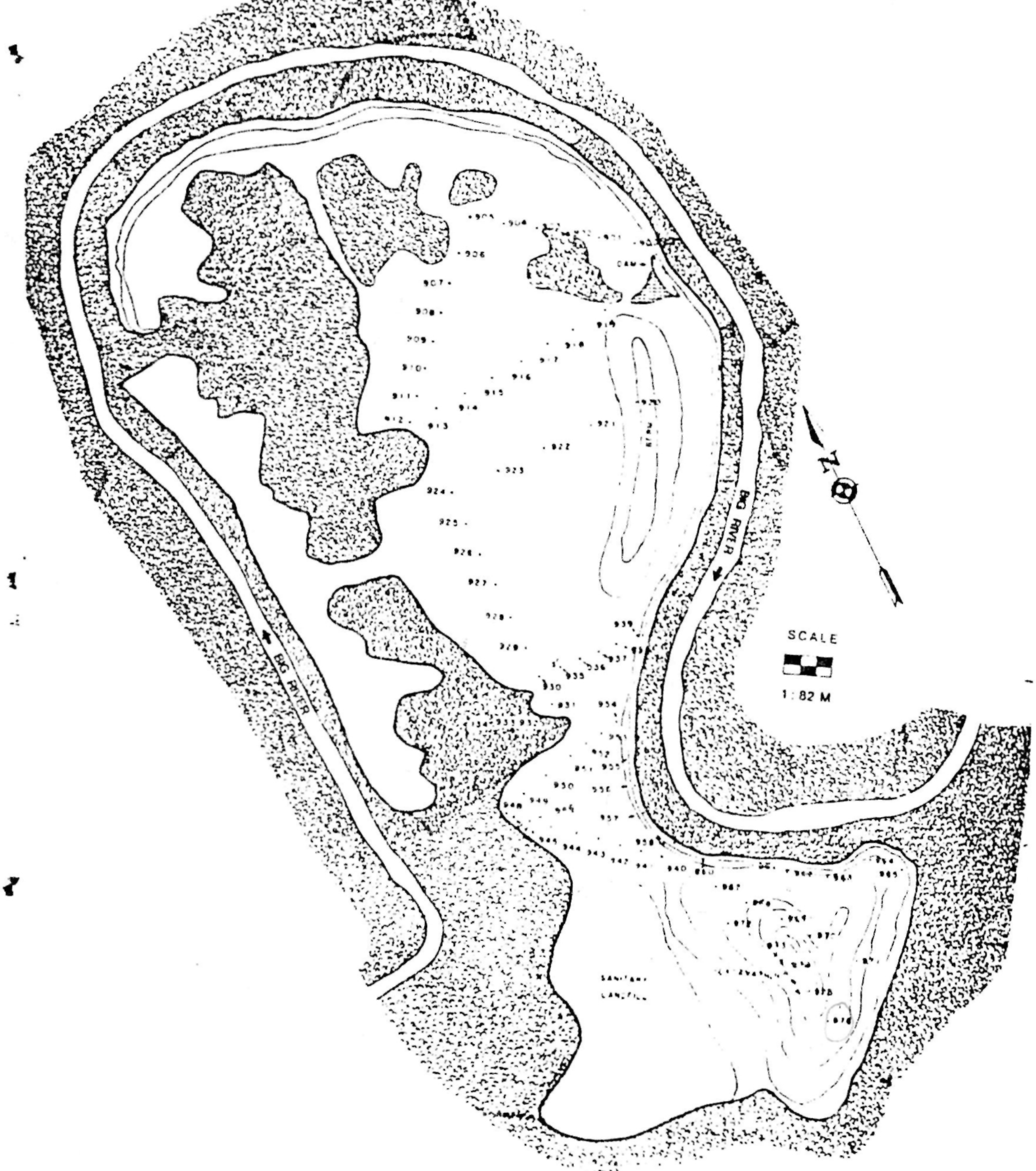


FIGURE 7. LOCATION OF SAMPLING SITES (BIG RIVER-DESLÔGE TAILINGS PILE).

TABLE 5

BIG RIVER-DESLOGE TAILINGS PILE

Sample No.	Metal Conc; ug/g Pb	Cd	Zn
D900	1670	37.8	1670
D901	1540	38.9	1700
D902	1420	27.4	1150
D903	1190	11.7	330
D904	1420	54.8	2380
D905	2590	30.2	1320
D906	3840	34.9	1750
D907	3560	26.5	1380
D908	970	6.8	875
D909	1250	15.6	950
D910	1800	15.7	1040
D911	1360	25	1080
D912	2310	40.0	1890
D913	4470	18.3	821
D915	1530	13.8	680
D916	826	15.7	531
D917	3140	31.7	1440
D918	1020	17.4	637
D919	958	21.4	798
D920	2710	29.9	1380
D921	1570	8.0	511
D922	997	7.0	406
D923	835	8.0	373
D924	896	7.5	437
D925	1310	9.8	373
D926	1080	13	297
D927	983	11.8	354
D928	877	16.5	518
D929	964	13.8	373
D930	1380	15.0	582
D931	1010	18.5	698
D932	1150	21.5	816
D933	951	11.6	233
D934	1620	20.5	840
D935	5530	46.9	404
D936	1570	24.2	933
D937	1400	8.7	525
D938	1330	19.8	733
D939	1140	21.5	783
D940	2380	19.2	1380
D941	1120	9.2	558
D942	1410	15.4	715
D943	4320	68.2	3580
D944	1800	15.8	1210
D945	1710	21.1	1090

TABLE 5 (Cont).
BIG RIVER-DESLOGE TAILINGS PILE

Sample No.	Metal Conc; ug/g Pb	Cd	Zn
D946	3190	17.5	1350
D947	933	12.0	344
D948	1440	13.5	439
D949	2380	18.1	644
D950	1730	15.9	693
D951	1540	55.9	519
D952	1490	7.7	560
D953	1070	24.5	1030
D954	4710	31.4	1510
D955	2780	30.7	1570
D956	5360	28.8	1330
D957	6200	37.3	1720
D958	2910	37.1	1680
D960	1880	35.8	3990 -
D961	1830	39.4	3080
D962	1950	38.9	2910
D963	1410	32.9	1970
D964	2180	45.6	2500
D965	2130	43.8	1780
D967	1980	37.8	1720
D968	2310	37.9	1870
D969	1810	25.6	1100
D970	3610	38.2	1850
D971	5822	46.2	2250
D972	2240	22.9	994
D973	4070	44.5	2090
D974	2110	33.6	1560
D975	3130	51.6	2410
D976	2690	78.6-	3970

An extensive study was carried out on the National tailings pile for this project and resulted in a thesis entitled "Impact of Tailings from Abandoned Lead Mines on the Water Quality and Sediments of Flat River Creek and Big River in Southeastern Missouri" by Mr. Larry E. Elliott (15).

Figure 8 indicates the location of the sampling sites on the National tailings pile used for this study. A total of ninety three samples of tailings material was collected and analyzed for lead, zinc, cadmium, and copper: seventy eight from the main pile, eight and seven from the erosion areas on the north and east sides, respectively as shown in Table 6. Table 7 provides a statistical analysis of the metal concentrations in each of the three areas.

Samples from the main pile were found to contain lead concentrations ranging from a low of 1640 ppm to a high of 9283 ppm, with values well distributed between these two extremes. Although samples taken in close proximity to one another often reflected similar concentrations with respect to the wide range of values encountered, no definite pattern seemed evident. The concentrations of lead appeared to be randomly dispersed from both the top to the bottom as well as around the perimeter of the pile. This random behavior was displayed by all four of the metals studied.

Zinc was found in concentrations generally ranging from 87 ppm to 978 ppm, with the exception of three samples which were found to be much higher. Two of these were just under 2000 ppm while the third, collected from the northwest side of the pile contained 5055 ppm of zinc.

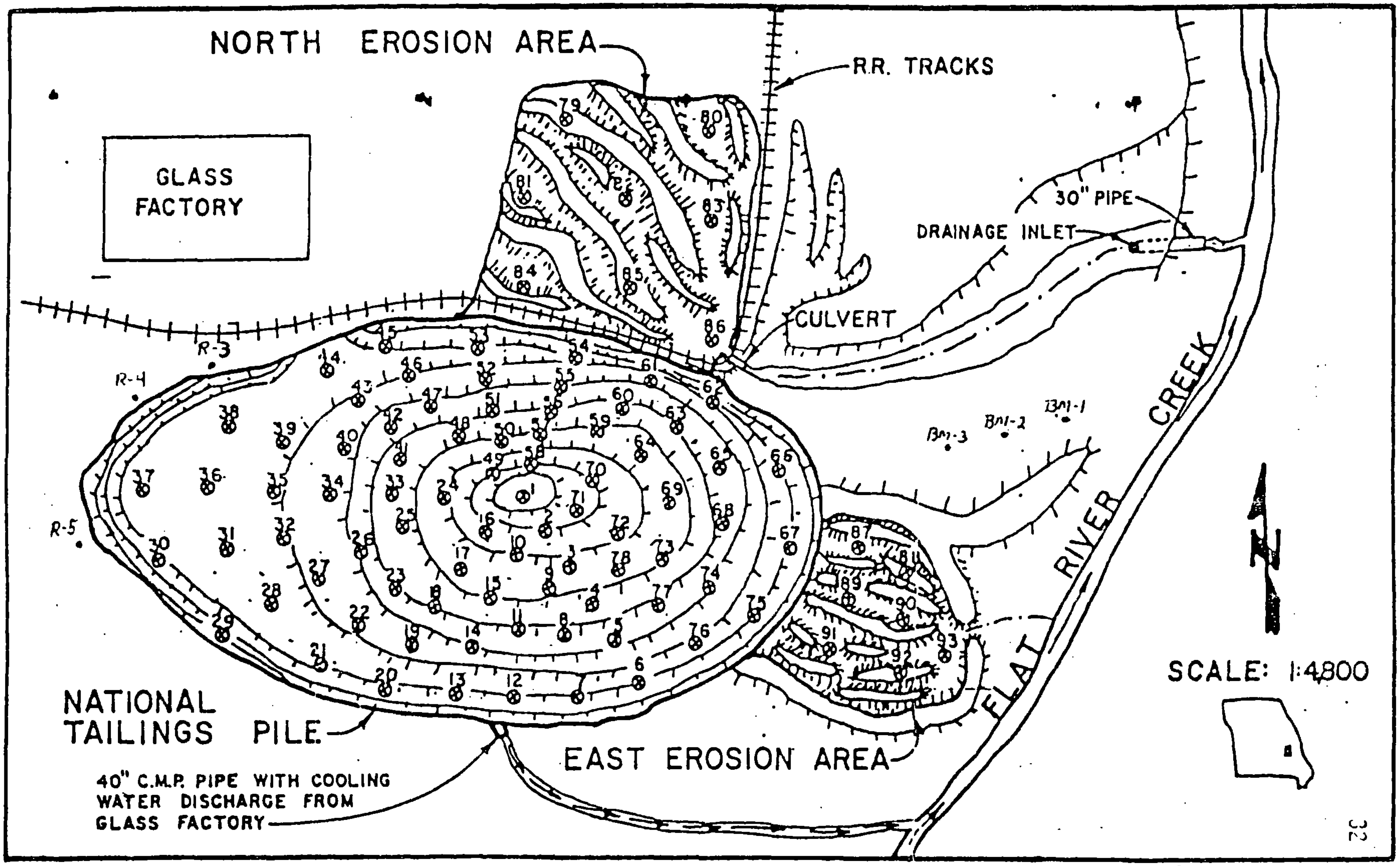


FIGURE 8. LOCATION OF SAMPLING SITES AT THE NATIONAL TAILINGS PILE (15).

TABLE 6
NATIONAL TAILINGS PILE (15)

Sample Number	Metals, ppm			
	Pb	Zn	Cd	Cu
1	5261	518	7	133
2	4225	305	6	122
3	1815	240	5	65
4	1959	108	4	95
5	2377	95	3	92
6	4780	238	3	190
7	4822	289	3	145
8	1822	87	3	196
9	2585	90	3	133
10	2348	258	5	91
11	4044	496	8	244
12	2581	432	7	264
13	4566	628	8	183
14	3881	703	9	176
15	5376	865	12	95
16	2579	156	4	64
17	3880	471	6	67
18	2396	174	5	165
19	3166	312	6	358
20	4327	955	13	197
21	3242	469	7	502
22	4762	621	9	354
23	2570	188	4	227

TABLE 6 (Cont.)
NATIONAL TAILINGS PILE (15)

Sample Number	Metals, ppm			
	Pb	Zn	Cd	Cu
24	2318	207	3	106
25	2413	722	11	63
26	2205	475	7	99
27	1678	454	7	154
28	4461	510	6	457
29	3504	436	5	229
30	4558	433	5	452
31	5341	547	6	426
32	2292	391	6	603
33	2189	245	4	91
34	1984	112	2	628
35	3007	314	4	215
36	3254	356	6	357
37	7101	1975	29	308
38	3519	403	6	339
39	2754	254	3	196
40	2854	237	3	109
41	2619	302	4	162
42	6446	1955	30	380
43	7766	5055	87	81
44	9283	626	10	182
45	2951	313	5	282

TABLE 6 (Cont.)
NATIONAL TAILINGS PILE (15)

Sample Number	Metals, ppm			
	Pb	Zn	Cd	Cd
46	5141	439	6	305
47	3512	363	5	130
48	4853	183	4	287
49	2283	95	3	67
50	4998	460	6	110
51	2635	289	5	114
52	3186	449	6	51
53	2203	267	6	241
54	2157	253	5	181
55	5333	397	6	90
56	2063	112	3	81
57	5060	408	6	135
58	5519	587	7	136
59	2380	176	4	131
60	2268	978	12	142
61	2093	232	4	101
62	4118	271	5	95
63	2724	379	5	107
64	3369	385	6	110
65	2240	329	6	101
66	2004	222	5	99
67	2962	302	5	137
68	1826	98	3	105

TABLE 6 (Cont.)
NATIONAL TAILINGS PILE (15)

Sample Number	Metals, ppm			
	Pb	Zn	Cd	Cu
69	4732	493	7	129
70	6759	609	7	131
71	3274	321	4	113
72	3465	211	4	121
73	2929	387	6	115
74	3646	277	4	101
75	2368	234	5	111
76	1640	127	3	139
77	3317	156	4	126
78	2694	115	4	91
79	2477	39	2	44
80	2192	102	11	32
81	5494	398	8	98
82	1553	107	4	88
83	1177	34	3	53
84	3229	70	3	39
85	2774	39	4	36
86	1183	107	4	99
87	4641	122	3	122
88	5204	129	4	286
89	7991	245	7	64
90	9245	135	4	183
91	7047	192	5	79

TABLE 6 (Cont.)
NATIONAL TAILINGS PILE (15)

Sample Number	Metals, ppm			
	Pb	Zn	Cd	Cu
92	8818	1170	19	459
93	6315	72	3	181

TABLE 7
STATISTICAL ANALYSIS OF HEAVY METALS
IN THE NATIONAL TAILINGS PILE (14)
Note: All Values in ppm

	Lead	Zinc	Cadmium	Copper
MAIN TAILINGS PILE				
Mean	3508	457	7.2	183
Standard Deviation	1516	613	10.1	124
95% Confidence Interval	$3172<\mu<3844$	$94<\mu<562$	$2.5<\mu<10.3$	$102<\mu<290$
NORTH EROSION AREA				
Mean	2510	112	4.9	61
Standard Deviation	1325	112	2.8	27
95% Confidence Interval	$1592<\mu<3428$	$29<\mu<190$	$3.0<\mu<6.8$	$42<\mu<80$
EAST EROSION AREA				
Mean	6894	295	6.4	196
Standard Deviation	1464	361	5.3	127
95% Confidence Interval	$5809<\mu<7979$	$94<\mu<562$	$2.5<\mu<10.3$	$102<\mu<290$

Cadmium was generally low in concentrations compared to the other three metals. With the exception of sample number fourty-three, containing eighty-seven ppm, all the samples contained concentrations of three to thirty ppm, inclusive. Sample number fourty-three exhibited the highest value of zinc, and contained nearly 8000 ppm of lead. This sample was also adjacent to the tailings sample showing the highest lead concentration.

Copper concentrations ranged from 51 ppm to a high of 628 ppm with the samples being well distributed throughout these limits. Of the four metals, copper seemed to be the most random in distribution, with samples in close proximity even differing greatly from one another.

Although no definite pattern was observed for the distribution of the metals throughout the pile, a sample abundant in one metal tended to have high concentrations of the others, with the exception of copper. For example, tailings materials rich in lead would likely be rich in zinc and cadmium.

The north erosion area displayed lower average concentrations for all four metals when compared with the main pile and the east erosion area. A lead pattern of dispersion not apparent for the main pile were evidenced in this area. Samples on the west and southwest edge of this area were highest in lead, followed by steadily decreasing concentrations as the sample sites progressed eastward.

Even though the highest value for zinc (398 ppm) and lead was shared by the same sample, the pattern of dispersion found for lead did not occur with zinc, cadmium, or copper. Zinc was found almost exclusively to fall within the interval of 34 ppm low to 107 ppm high.

The values for cadmium ranged from 2 to 11 ppm, while copper ranged from 32 ppm to 99 ppm.

Unlike material from the main pile, samples in the north erosion area that were rich in one metal did not generally correspond to high concentrations in any of the other three metals.

The east erosion area contained the highest average concentrations for lead and copper and demonstrated a pattern of dispersion for lead, while zinc, cadmium, and copper failed to exhibit a recognizable pattern.

Lead, up to a high value of 8818 ppm on the southern portion of the erosion area, and a low of 4641 ppm on the northern portion, tended to increase in concentration as the sample points progressed southward. The sample points going from east to west, however, differed only slightly in their respective concentraticns of lead.

Hand augered samples to a depth of 8 feet were made by the U.S. Bureau of Mines team for the north and east erosion area. Samples number BM-1, BM-2 and BM-4 were made in the tailings runoff area affected by storm water that ultimately drain into Flat River Creek to the east of the deposit. Augered samples were also taken in the vicinity of samples number 82, 89 and 90 in the erosion areas.

Rotary core samples were taken to the bottom of the tailings piles at locations R-3, R-4 and R-5. All of these locations are noted in Figure 8. Table 8 indicates the augar and core samples by depth with concentraions of Pb, Cd and Zn. Table 9 gives the ICAP data for elements found at different depths for the R-3 and R-4 coring sites. Table 10 gives the rotary core ICAP analysis for site R-5 down to the clay layer underlying the pile at a depth of approximately eleven feet.

TABLE 8
AUGER AND CORE SAMPLES ON NATIONAL
TAILINGS PILE (Courtesy of Bureau of Mines)

Sample No.		Metal Conc; ug/g		
		Pb	Cd	Zn
Hand Augered				
BM-1	Surface	1100	40	700
BM-1	2 ft	4100	20	300
BM-1	4 ft	4600	30	400
BM-2	Surface	4700	30	400
BM-2	2 ft	3800	30	300
BM-2	4 ft	2000	40	300
BM-3	Surface	2700	40	300
BM-3	2 ft	1900	40	200
BM-3	4 ft	1500	40	200
89	2 ft	2800	01.0	76
89	4 ft	3400	01.4	74
90	Surface	1800	2	78
82	2 ft	2100	1	28
82	4 ft	1100	5	270
82	6 ft	1200	3	150
82	8 ft	1200	1	40
82	Gully Side	760	1	42
Rotary Cored				
R-3	3 ft	7400	45	2700
R-3	5 ft	1400	15	1200
R-4	2-5 ft clay	6400	26	1200
R-4	3 ft chat	10200	72	3400
R-5	3 ft	9700	76	3700
R-5	6 ft	7100	120	6300
R-5	9 ft	8600	80	4100
R-5	10 ft	8300	88	5000
R-5	11 ft bottom clay	820	220	330

TABLE 9
ROTARY CORE SAMPLING OF NATIONAL TAILINGS DEPOSIT. INDUCTIVE COUPLED ARGON PLASMA ANALYSIS (ICAP) FOR SITES R-3 AND R-4 BY DEPTH
(UNITS ARE MICROGRAMS/GRAM)

	R-3		R-4	
Element	3 ft	5 ft	2.5 ft	3 ft
Ag	9.	4.	8.	7.
Al	3500.	16,000.	1300.	8000.
As	<2.	<8.	8.	<2.
B	6.	<8.	3.	7.
Ba	29.	104.	8.1	66.
Be	1.2	0.73	1.5	0.92
Ca	140,000.	31,000.	170,000.	130,000.
Cd	45.	15.	72.	26.
Co	150.	30.	180.	61.
Cr	9.5	26.	3.9	10.
Cu	58.	45.	96.	29.
Fe	34,000.	30,000.	41,000.	29,000.
Li	4.	8.	2.	7.
Mg	69,000.	16,000.	84,000.	70,000.
Mn	3800.	2300.	4600.	3400.
Mo	40.	<8.	50.	40.
Ni	97.	31.	150.	56.
P	260.	320.	270.	280.
Sb	<3.	<17.	<3.	<3.
Se	50.	<17.	30.	30.
Si	180.	410.	86.	450.
Sn	<2.	<8.	<2.	<2.
Sr	32.	12.	37.	35.
Ti	20.	180.	<0.3	54.
V	10.	39.	5.	18.
Zn	2700.	1200.	3400.	1200.

TABLE 10
ROTARY CORE SAMPLING OF NATIONAL TAILINGS DEPOSIT
INDUCTIVE COUPLED ARGON PLASMA (ICAP) ANALYSIS FOR
SITE R-5 BY DEPTH
(UNITS ARE MICROGRAMS/GRAM)

Element	3 ft	6 ft	9 ft	10 ft	BOTTOM CLAY 11 ft
Ag	10.	10.	8.	8.	0.7
Al	1100.	1100.	1500.	1800.	4200.
As	6.	6.	9.	20.	20.
B	20.	<2.	10.	7.	3.
Ba	4.5	5.9	7.2	13.	19.
Be	1.5	1.4	1.5	1.2	0.2
Ca	180,000.	170,000.	170,000.	160,000.	98,000.
Cd	76.	120.	80.	88.	220.
Co	78.	76.	93.	100.	4.8
Cr	3.2	7.0	14.	22.	6.
Cu	130.	72.	99.	83.	6.8
Fe	39,000.	31,000.	35,000.	34,000.	6400.
Li	2.	2.	3.	2.	3.
Mg	90,000.	86,000.	85,000.	81,000.	57,000.
Mn	4700.	4300.	4400.	4200.	550.
Mo	50.	40.	50.	40.	<2.
Ni	67.	49.	72.	77.	6.0
P	280.	360.	340.	370.	90.
Sb	<3.	<3.	<3.	<3.	<3.
Se	30.	30.	40.	30.	<3.
Si	130.	220.	130.	130.	170.
Sn	<2.	<2.	<2.	<2.	<2.
Sr	40.	40.	<0.03	38.	30.
Ti	<0.3	<0.3	<0.3	2.	32.
V	4.	4.	5.	7.	11.
Zn	3700.	6300.	4100.	5000.	330.

The samples BM-1, BM-2 and BM-4 in the drainage pattern reflect the tailings transport from the north erosion area and part of the main dome-like structure of the main pile. The lower lead values shown for the two erosion areas reflect the slime pool discharges that had more of the lead removed during processing.

The rotary core samples were made along the edge of the older chat material at the western side of the main tailings pile. It was known that the chat material in this area averaged around 8000 to 10,000 ppm lead and we wanted to determine what the depth of the chat materials was in this area. The deposit turned out to be thinner than thought in most areas (3-5 feet deep) where people had been hauling the chat away for road material or use as agricultural limestone. The clay layer underlying the deposit had low lead and zinc values but increased cadmium levels (up to 220 ppm) which were significantly higher than concentrations normally found in the tailings, chat or slime line materials.

Water brought up with the core samples did not exhibit an anaerobic or methane odor again suggesting that rainwater percolates through the chat and tailings materials and then moves horizontally along the top of the clay materials and drains into Flat River Creek.

D. Elvins

The Elvins tailings pile borders northern Elvins, Missouri and covers a land area of approxiamtely 0.6 square km (0.25 square miles). Two shallow lakes are found on the southwestern edge of the tailings pile and seepage from the base of the deposit passes through these shallow lakes and then flows into Flat River Creek. These waters contain high levels of dissolved calcium, magnesium, zinc and lead which have an impact on the sediments and biota of Flat River Creek.

The Elvins tailings pile was studied in 1976 by Kramer (16) and the growth of algae in the zinc rich wastes and seepage water has been reported by Whitton, et al (17). Presently a small asphalt paving plant operates on the southern perimeter of the tailings pile with the tailings being used as a finer sized aggregate source.

Figure 9 illustrates the location of 91 sampling sites on the Elvins tailing pile. Table 11 gives the metal concentrations of Pb, Cd and Zn found at the sampling locations.

E. Bonne Terre

The Bonne Terre tailing deposits consist of two different areas and configurations. A large chat and tailings dome is situated on the east side of Bonne Terre, Missouri and covers an area of approximately 50 acres of land. The second area is located about 1/2 mile to the west of the chat hill just across Missouri Highway 67 and is a mostly dried-up tailings pond covering about 272 acres.

Figure 10 gives the location of sampling sites on the Bonne Terre tailings pile which is shaped like a small hill overlooking a golf course. Table 12 lists the metal concentrations found for Pb, Cd and Zinc at the tailings pile.

Figure 11 shows the location of sampling sites on the flat tailings deposits of the Bonne Terre east deposit which still has water confined at one end. Table 13 gives the metal concentrations found for Pb, Cd and Zn at the recorded sampling locations.

F. Statistical Analysis of Different Tailings Piles

Heavy metal data from the characterization of the different tailings and chat piles studied were statistically evaluated for

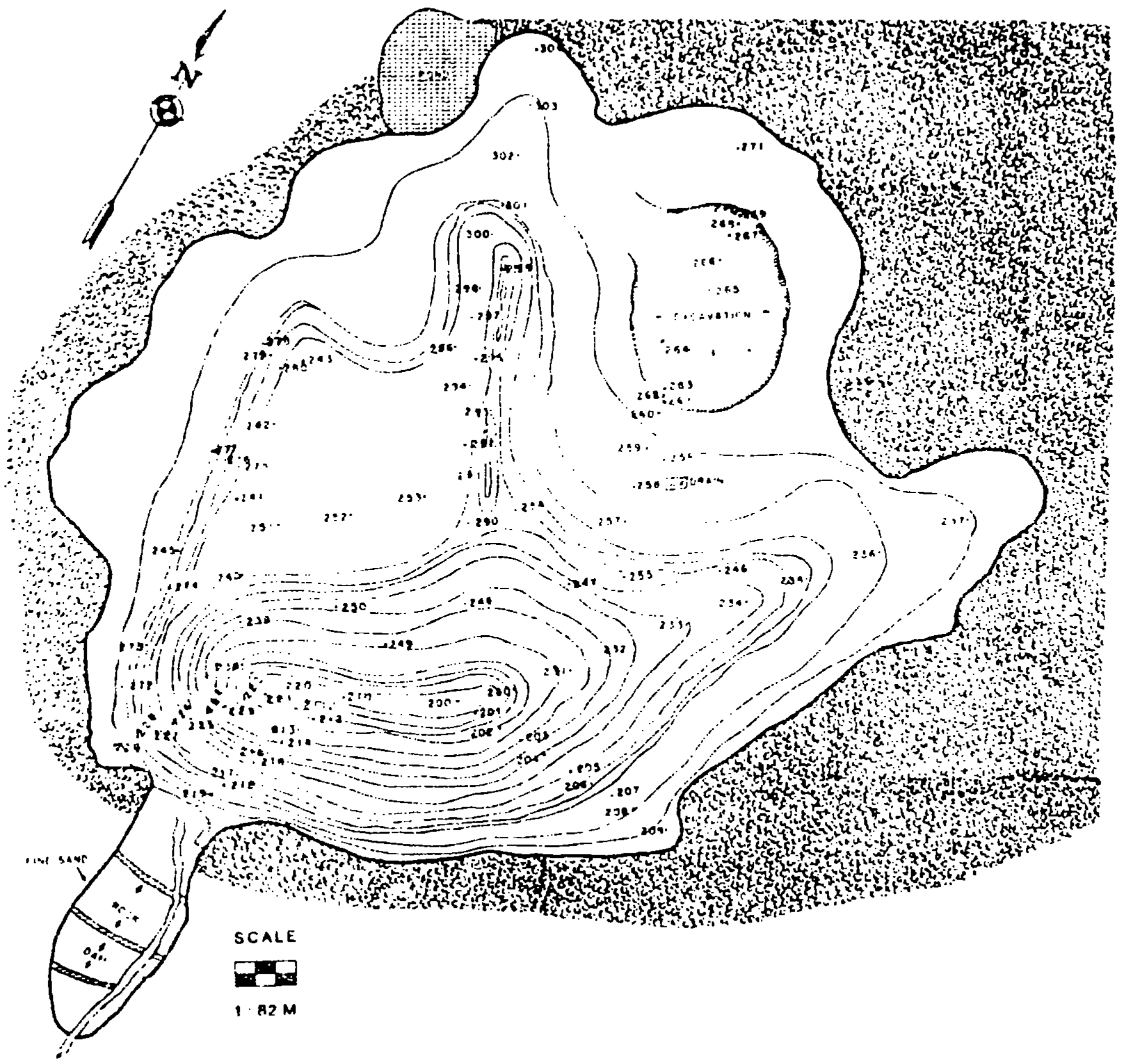


FIGURE 9. LOCATION OF SAMPLING SITES ON ELVINS TAILINGS PILE.

TABLE - 11
ELVINS TAILINGS PILE

Sample No.	Metal Conc; ug/g Pb	Cd	Zn
E200	5990	190	6100
E201	6420	180	11200
E202	7950	202	11200
E203	5130	199	10600
E204	4460	165	9210
E205	4200	156	8620
E206	4400	168	9510
E207	3570	140	8210
E208	3650	152	8180
E210	5180	171	11800
E211	4190	179	11400
E212	6000	153	9600
E213	4630	160	9630
E214	5450	155	8610
E215	6780	156	8080
E216	6960	172	9260
E217	5240	120	6870
E218	4980	114	6000
E219	7500	106	5600
E220	4760	168	10500
E221	6820	163	11400
E222	5500	110	6400
E223	5990	114	6100
E224	4470	70.8	4350
E225	5270		8590
E226	4010	92.9	5320
E227	1880	51.5	1290
E228	3680	84.6	5150
E229	5180	132	6480
E230	4550	76.3	6540
E231	4300	189	11900
E232	3880	138	8820
E233	3170	151	2040
E234	2780	126	6510
E235	3630	112	6090
E236	3180	92.5	4560
E237	1300	79.6	4470
E238	8140	106	1760
E239	8360	135	9280
E240	6200	84.0	4290
E241B	8000	95.0	1300
E242	9600	157	10900
E245	11100	91.8	4950
E246	5640	161	9680
E247	7080	159	8360
E248	3780	144	7870
E249	4600	129	6990

TABLE - 11 (Cont.)
ELVINS TAILINGS PILE

Sample No.	Metal Conc; ug/g Pb	Cd	Zn
E250	6410	138	2040
E251	6190	114	6290
E252	4850	127	7020
E253	4050	118	6340
E254	4440	115	5360
E255	1700	51.3	2480
E256	2750	52.8	2210
E257	1350	48.3	2290
E258	1170	45.0	2190
E259	2180	54.4	2440
E260	2750	69.8	3300
E261	1060	61.4	2170
E262	1400	110	5500
E263	1270	74.8	3570
E264	1120	72.2	3230
E265	1620	75.5	3770
E266	4230	119	1440
E267	1060	74.7	3620
E268	1050	74.8	3660
E269	991	58.2	2140
E270	851	57.9	2600
E271	1100	74.7	2650
E272	4190	82.3	4240
E273	8890	85.0	4250
E274	4890	63.9	3290
E275	7160	100	4810
E276	9310	19.8	792
E277	9260	31.5	1950
E278	10000	134	8510
E279	11600	163	10900
E280	7200	94.4	5960
E290	4020	62.9	3510
E291	2750	56.1	3000
E292	2890	50.2	2330
E293	1080	41.7	2450
E294	2940	67.6	3380
E295	2190	75.8	3980
E296	2230	99.1	5820
E297		59.3	3600
E298	1890	48.4	2610
E299	3160	61.7	3210
E300	2270	47.3	2360
E301	2080	54.4	2230
E302	1780	42.2	1990
E303	1650	44.9	2120
E304	1900	42.6	108

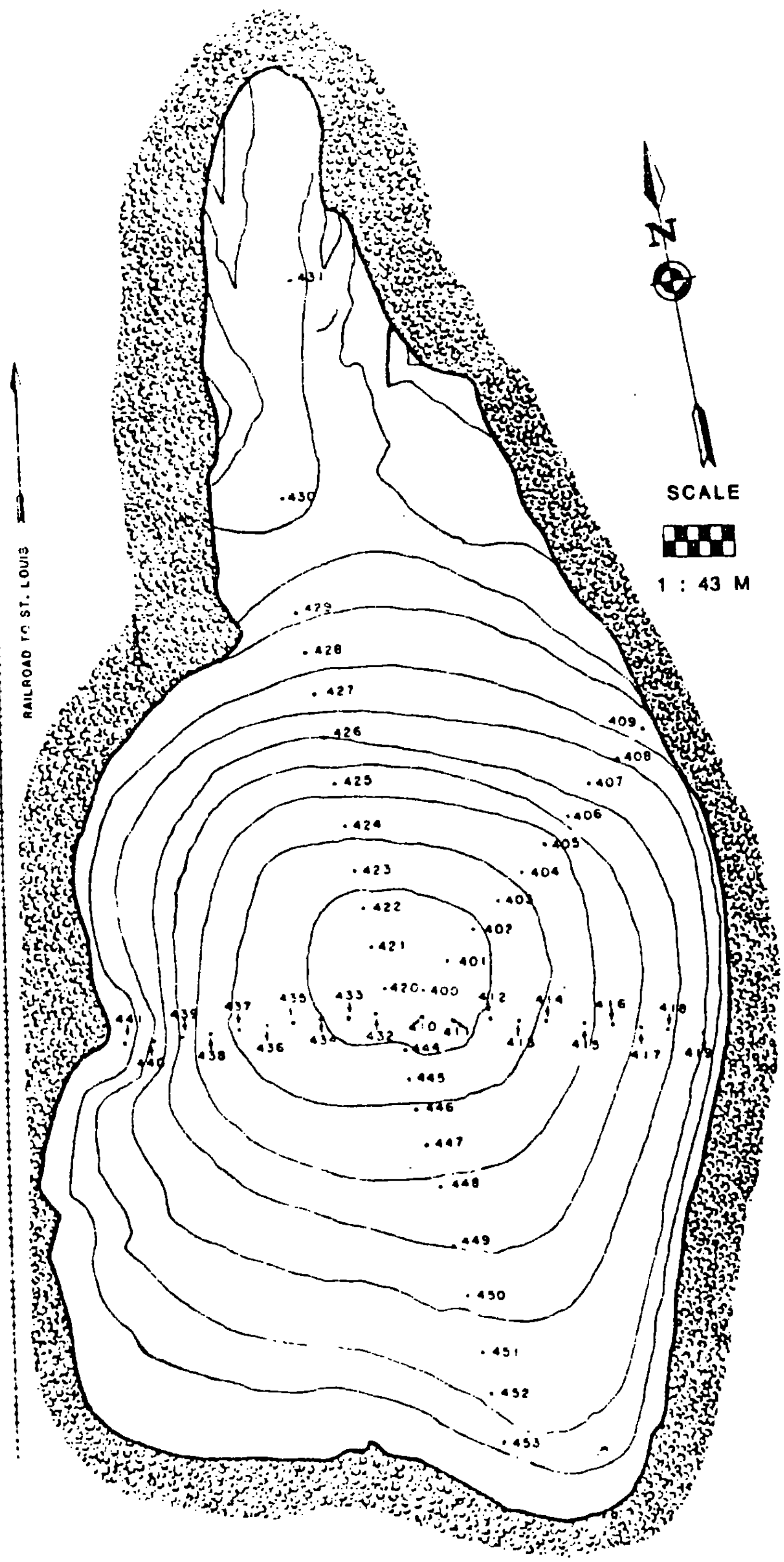


FIGURE 10. LOCATION OF SAMPLING SITES ON BONNE TERRE TAILINGS PILE.

TABLE - 12
BONNE TERRE TAILINGS PILE

Sample No.	Metal Conc; ug/g Pb	Cd	Zn
BT400	5330	9.7	469
BT401	5020	5.4	273
BT402	1300	10.2	309
BT403	2020	9.9	430
BT404	2280	11.7	451
BT405	3540	11.9	689
BT406	3070	12.1	718
BT407	1890	17.6	650
BT408	1540	12.3	587
BT409	3230	14.9	501
BT410	3590	13.9	51.3
BT411	4120	13.4	671
BT412	4450	17.7	757
BT413	3140	14.4	722
BT414	4350	12.0	309
BT415	2540	16.1	757
BT416	3040	16.4	648
BT417	1630	9.6	486
BT418	1840	13.7	597
BT419	1760	10.0	641
BT420	1480	3.0	150
BT421	3080	5.5	194
BT422	2050	13.3	434
BT423	1940	13.0	479
BT424	2190	13.5	458
BT425	2380	15.1	573
BT426	2390	17.2	622
BT427	1580	15.1	553
BT428	1860	14.2	686
BT429	1340	13.9	661
BT430	4720	29.5	786
BT431	2650	7.0	150
BT432	3200	15.2	705
BT433	3200	15.8	650
BT434	7010	8.2	426
BT435	6670	15.3	477
BT436	5820	10.9	361
BT437	5210	18.1	559
BT438	4290	11.5	573
BT439	6730	13.6	755
BT440	6840	12.8	618
BT441	5800	16.0	180

TABLE - 12
BONNE TERRE TAILINGS PILE

Sample No.	Metal Conc;.ug/g Pb	Cd	Zn
BT444	3280	15.1	511
BT445	4530	13.6	444
BT446	4220	17.4	697
BT447	5030	19.2	746
BT448	5980	22.5	967
BT449	5190	28.8	623
BT450	3390	22.4	922
BT451	3540	22.0	878
BT452	2791	15.7	563
BT453	6230	10.4	539

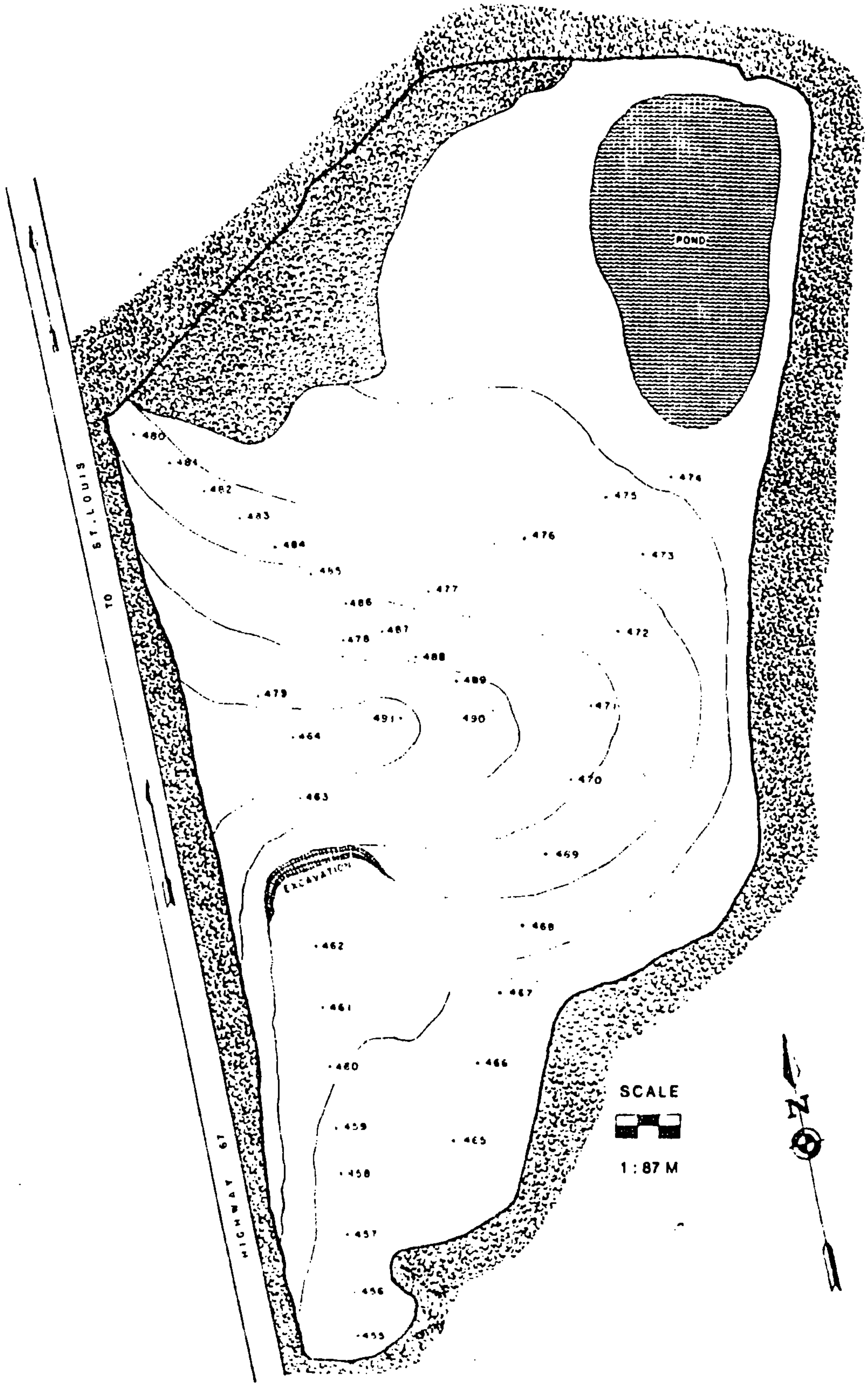


FIGURE 11. LOCATION OF SAMPLING SITES ON BONNE TERRE TAILINGS FLAT.

TABLE 13
BONNE TERRF TAILINGS FLAT

Sample No.	Metal Conc; ug/g		
	Pb	Cd	Zn
BT455	1232	5.9	173
BT456	3020	10.2	361
BT457	6650	10.5	312
BT458	1810	5.9	385
BT459	1600	9.0	354
BT460	1920	12.3	491
BT461	1170	9.3	312
BT462	1610	10.0	234
BT463	989	8.4	185
BT464	1560	7.3	205
BT465	1550	11.2	244
BT466	2310	12.0	380
BT467	1540	10.8	366
BT468	3450	10.4	243
BT469	1620	9.5	255
BT470	1860	6.0	157
BT471	1520	4.5	87.2
BT472	2710	6.3	222
BT473	1170	3.6	99.5
BT474	660	7.9	151
BT475	1440	4.7	156
BT476	2610	4.9	330
BT477	1320	6.0	165
BT478	1900	13.2	337
BT479	1760	9.8	273
BT480	1290	13.8	524
BT481	1480	15.1	543
BT482	1780	13.3	321
BT483	1820	5.6	618
BT484	1400	6.7	171
BT485	2840	10.0	1470
BT486	7610	20.9	698
BT487	1590	6.7	152
BT488	1020	6.4	115
BT489	1950	8.1	321
BT490	1120	5.2	170

differences in Pb, Cd and Zn. Table 14 shows the results of this evaluation. The chat and tailings piles may be segregated by metal composition and this information could be most useful in considering stabilization, use as agricultural limestone or for road material, or for possible contributions to sediments of the Big River through stormwater runoff.

The east erosion area of the National tailings pile contained the highest mean average of 6894 ppm Pb but a low Cd and Zn concentration. The Elvins pile contained the second highest mean lead values of 4392 ppm coupled with the highest zinc values of 5482 ppm.

The Leadwood deposit contained the highest cadmium values of 267 ppm coupled with the second highest zinc values of 5009 ppm. It was of interest to note that the Big River-Desloge pile has the lowest mean lead values of 2077 coupled with average cadmium and zinc concentrations.

These concentrations of metals may be compared with the values found in tailings from the Viburnum Trend or New Lead Belt with an average of 320 ppm lead, 8 ppm cadmium and 500 ppm zinc reflecting the increased efficiency of the flotation process presently in use by the mining industries.

These values help to explain, in part, the impact due to the physical transport of tailings materials on Big River and Flat River Creek. These impacts had been studied by Zachritz (18) and others (12) concerned with the concentrations and distribution of heavy metals in the sediments of the Big River which have contributed to a problem with lead in tissues of bottom feeding suckers (19).

TABLE 14
STATISTICAL ANALYSIS OF HEAVY METALS
IN THE DIFFERENT TAILINGS PILES

	LEAD	CADMIUM	ZINC
LEADWOOD			
Mean	2444	267	5009
Standard Deviation	4072	394	4894
95% Confidence Interval	2455<u<3231	223<u<299	4957<u<5894
Maximum	17000	1870	25800
Minimum	597	9.3	633
BIG RIVER DESLOGE			
Mean	2077	26	1226
Standard Deviation	1294	15.2	860
95% Confidence Interval	1931<u<2224	24<u<28	1129<u<1323
Maximum	6200	78.6	3990
Minimum	826	6.8	233
NATIONAL			
Mean	3508	7.2	457
Standard Deviation	1516	10.1	613
95% Confidence Level	3172<u<3844	2.5<u<10.3	94<u<562
1) NORTH EROSION AREA			
Mean	2510	4.9	112
Standard Deviation	1325	2.8	112
95% Confidence Interval	1592< u<3428	3.0<u<6.8	29<u<190
2) EAST EROSION AREA			
Mean	6894	6.4	295
Standard Deviation	1464	5.3	361
95% Confidence Interval	5809<u<7979	2.5<u<10.3	94<u<562
ELVINS			
Mean	4392	103	5482
Standard Deviation	2581	47.1	3179
95% Confidence Interval	4130<u<4654	98<u<108	5160<u<5803
Maximum	11600	202	11900
Minimum	851	19.8	108
BONNE TERRE			
Mean	3515	13.9	541
Standard Deviation	1705	5.3	211
95% Confidence Interval	3285<u<3744	18.2<u<14.6	512<u<569
Maximum	7010	29.5	967
Minimum	1300	3.0	51.3

Elliott (15) and Wixson _et al_. (12) have noted that the tailings materials tend to move downriver during storm events with the heavier metal rich fraction tending to settle out first as the storm water event decreases. This accounts for pulses of metals that may be found at different locations following periods of elevated rainfall and rapid runoff into and down the Big River.

Considering the amount of sediments found in the intestines of bottom feeding suckers, the bioavailability of lead and other metals in the sediments is rather small. However, continued monitoring is needed to make sure that lead levels in edible fish tissues do not approach levels of concern to human health.

VI. FIELD STUDIES OF TAILINGS USED FOR AGRICULTURAL LIMESTONE PURPOSES

One of the objectives of this research project was to sample, analyze and evaluate soil and vegetation in a natural field environment where tailings material had been used for agricultural limestone over a period of years. With the assistance of Mr. John Carter, Environmental Engineer, St. Joe Minerals Corporation and the permission of Mr. T. Ferguson, a series of such samples were taken on the Ferguson farm near Farmington, Missouri.

At this site a random survey was made of the soil using the standard "staggered W" method. Each sample was comprised of 20 auger cores to a depth of 10 cm and bulked into a polyethylene bag. Soil samples were then dried at air temperature in the laboratory, ground and passed through a nylon sieve of 2 mm aperature.

Vegetation samples of grass and clover were collected with stainless steel implements at appropriate soil sampling sites and placed in polyethylene bags with the root system intact in the soil sample. In the laboratory, the plant material was separated from the soil and carefully washed by standard methods and dried at 100^{o}C followed by milling and analysis.

Analysis for the soil samples was by AAS (flame or graphite furnace) or ICAP performed by the Environmental Trace Substances Research Center at the University of Missouri in Columbia, Missouri. Appropriate preparation, extraction and control techniques were employed in the analysis of the soil and plant material.

Figure 12 illustrates the "staggered W" sampling scheme and sample site locations within the confines of the Ferguson farm. Table 15 gives the ICAP analysis for soils, grass, leaves, stems and roots; and clover flowers, leaves and roots. These data are important to determine how much metal (such as lead) might be removed from the tailings amended soil and translocated into the roots, stems, leaves or flowers of grass and clover grown in the field for animal consumption. Additional elements determined by the ICAP method are also listed for the soil and vegetation sampled. Units reported are micrograms/gram (dry weight for plant materials).

Table 16 indicates the soil analysis (AAS) for sample sites on the Ferguson farm where grass or clover samples were not collected.

The Ferguson farm pasture studied was last limed with tailings from the Big River-Desloge tailings pile in 1978 according to information received from Mr. Ferguson. Tailings from other locations had also been used on this seventeen acre field for a number of years preceeding the 1978 application.

The highest lead soil value found was 200 μg/g and the grass growing in this material gave an analysis of 40 for the roots, 4 for the stems and 13 in the blade portion of the grass. At sample site number 420 the soil contained 100 μg/g Pb and the grass roots reflected 100 μg/g with 2 in the stem and 5 found in the blades or leaves.

The clover plants had even less accumulation of lead or other metals in the roots, stems, leaves or flowers of the plant growing on the tested soil.

TABLE 15

SOIL AND VEGETATION ANALYSIS (ICAP) FOR SAMPLE SITES ON FERGUSON FARM (UNITS IN MICROGRAMS/GRAM)

Element	419 Soil	420 Soil	420 Grass Leaves	420 Grass Stems	420 Grass Roots
Ag	<0.3	<0.3	0.4	< 0.3	<0.2
Al	5300.	8500.	130.	190.	4100.
As	10.	10.			
B			5.2	4.	4.
Ba	63.	66.	9.8	7.0	45.
Be	0.49	0.46	<0.03	<0.03	0.44
Ca	6400.	12000.	4500.	1700.	27000.
Cd	0.7	0.9	0.3	<0.3	1.4
Co	8.0	9.3	0.3	0.5	7.2
Cr	13.	13.	0.88	0.7	17.
Cu	34.	28.	5.8	4.	27.
Fe	12000.	12000.	150.	210.	17000.
K	290.	530.	14000.	9800.	2400.
Li	3.4	6.6	<0.3	<0.3	2.4
Mg	3400.	6600.	3500.	2100.	13000.
Mn	720.	740.	81.	77.	1100.
Na	23.	42.	230.	160.	600.
Ni	5.6	9.5	0.8	0.8	5.5
P	270.	540.	3300.	2500.	1100.
Pb	78.	100.	4.9	2.	100.
Si	48.	54.	220.	170.	43.
Sr	4.8	9.1	6.6	3.4	12.
Ti	19.	66.	1.5	3.1	93.
V	23.	24.	0.3	0.5	27.
Zn	32.	56.	14.	23.	70.

TABLE 15 (Cont.)

Element	421 Soil	421 Clover Roots	421 Clover Stems	421 Clover Flowers	421 Clover Leaves
Ag	<0.3	<0.6	<0.2	0.3	<0.4
Al	6000.	1600.	<2.	53.	40.
As	10.				
B		9.	19.	29.	16.
Ba	67.	32.	23.	11.	18.
Be	0.46	0.07	<0.02	<0.02	<0.04
Ca	14000.	5400.	7500.	12000.	19000.
Cd	1.0	<1.	<0.2	0.6	<0.4
Co	8.2	3.0	0.3	1.1	0.8
Cr	13.	3.9	<0.2	2.5	0.4
Cu	18.	34.	5.3	28.	16.
Fe	11000.	2900.	41.	94.	150.
K	420.	4400.	6600.	13000.	7400.
Li	4.5	1.2	<0.2	<0.2	<0.4
Mg	7300.	6600.	6500.	3800.	3900.
Mn	780.	260.	19.	81.	150.
Na	40.	800.	54.	120.	110.
Ni	7.1	1.5	0.95	3.8	9.3
P	690.	2900.	1300.	2900.	1800.
Pb	100.	12.	<1.	3.	8.8
Si	360.	230.	<0.5	<0.8	0.8
Sr	11.	17.	20.	14	20.
Ti	35.	24.	<0.2	<0.2	<0.4
V	21.	8.0	<0.2	<0.2	<0.4
Zn	70.	45.	13.	780.	53.

TABLE 15 (Cont.)

Element	425 Soil	425 Grass Roots	425 Grass Stems	425 Grass Leaves	425 Clover Roots
Ag	<0.3	0.3	1.	<0.4	0.5
Al	8100.	2500.	80.	350.	330.
As	10.				
B		6.	<4.	6.	16.
Ba	76.	42.	12.	15.	15.
Be	0.54	0.3	<0.07	<0.04	<0.05
Ca	16000.	24000.	2100.	3500.	2800.
Cd	2.8	7.0	<0.7	0.6	0.5
Co	8.6	6.2	<0.7	0.9	0.7
Cr	12.	10.	1.	1.6	1.
Cu	15.	24.	4.6	8.4	23.
Fe	10000.	8300.	120.	390.	400.
K	660.	2500.	22000.	27000.	5600.
Li	6.3	1.5	<0.7	<0.4	<0.5
Mg	8800.	12000.	3400.	3700.	5900.
Mn	980.	1000.	60.	74.	60.
Na	45.	540.	190.	270.	1100.
Ni	10.	6.0	1.	2.3	1.
P	450.	1100.	4200.	4400.	3400.
Pb	200.	40.	<4.	13.	5.
Si	44.	410.	<1.	310.	30.
Sr	9.9	11.	3.6	5.2	10.
Ti	78.	33.	2.6	16.	3.3
V	22.	16.	0.8	1.	2.3
Zn	120.	410.	45.	27.	22.

TABLE 15 (Cont)

Element	425 Clover Stems	425 Clover Flowers	425 Clover Leaves	425 Soil
Ag	0.3	<2.	<0.2	<0.3
Al	9.	<20.	40.	8100.
As				10.
B	22.	10.	28.	
Ba	20.	7.3	12.	76.
Be	<0.02	<0.2	<0.02	0.54
Ca	6400.	12000.	18000.	16000.
Cd	0.3	<2.	0.3	2.8
Co	<0.2	<2.	0.4	8.6
Cr	0.4	<2.	0.4	12.
Cu	6.1	14.	14.	15.
Fe	48.	91.	120.	10000.
K	9400.	21000.	13000.	660.
Li	<0.2	<2.	<0.2	6.3
Mg	3700.	3200.	3600.	8800.
Mn	16.	66.	92.	980.
Na	55.	150.	91.	45.
Ni	0.5	2.	1.3	10.
P	1700.	4400.	2500.	450.
Pb	<1.	<8.	2.	200.
Si	<0.5	<3.	0.6	44.
Sr	17.	8.5	14.	9.9
Ti	<0.2	<2.	<0.2	78.
V	<0.2	<2.	<0.2	22.
Zn	14.	49.	43.	120.

TABLE 15 (Cont)

Element	429 Soil	429 Grass Roots	429 Grass Stems	429 Grass Leaves
Ag	<0.3	<0.3	<0.3	0.4
Al	4400.	2300.	110.	180.
As	10.			
B		<2.	<1.	6.
Ba	71.	33.	19.	14.
Be	0.62	0.30	<0.03	<0.04
Ca	22000.	18000.	2400.	3800.
Cd	2.2	1.3	0.88	<0.4
Co	13.	6.1	0.6	0.4
Cr	9.6	6.6	2.2	1.
Cu	33.	25.	7.9	7.0
Fe	13000.	6800.	160.	200.
K	410.	4900.	25000.	39000.
Li	3.1	1.6	<0.3	<0.4
Mg	11000.	9200.	2700.	4100.
Mn	1200.	690.	54.	57.
Na	42.	490.	170.	230.
Ni	7.8	4.2	2.3	1.5
P	620.	1200.	3100.	5200.
Pb	160.	68.	2.	6.6
Si	230.	58.	170.	300.
Sr	9.5	9.9	5.0	6.9
Ti	30.	50.	2.9	3.0
V	20.	14.	0.5	0.5
Zn	93.	120.	36.	23.

TABLE 15 (Cont)

Element	430 Soil	430 Grass Roots	430 Grass Leaves	430 Grass Stems
Ag	<0.3	<0.3	<0.3	<0.3
Al	6500.	2600.	130.	150.
As	26.			
B		4.	<2.	4.5
Ba	76.	40.	13.	14.
Be	0.66	0.15	<0.03	<0.03
Ca	17000.	9000.	3400.	1900.
Cd	2.0	0.8	<0.3	0.4
Co	14.	6.8	0.4	0.5
Cr	12.	5.0	0.4	0.6
Cu	22.	40.	7.5	5.6
Fe	13000.	4900.	180.	180.
K	580.	4700.	32000.	17000.
Li	5.1	1.6	<0.3	<0.3
Mg	9000.	4200.	3600.	1900.
Mn	1100.	620.	59.	53.
Na	39.	380.	250.	120.
Ni	8.9	3.8	0.4	0.7
P	550.	1100.	4500.	2500.
Pb	120.	27.	3.	2.
Si	27.	42.	260.	210.
Sr	8.8	7.5	6.2	3.8
Ti	30.	52.	2.7	3.7
V	23.	12.	0.3	0.6
Zn	110.	130.	21.	32.

TABLE 15 (Cont)

Element	430 Soil	430 Clover Leaves	430 Clover Roots	430 Clover Stems
Ag	<0.3	<0.3	<0.2	<0.2
Al	6500.	190.	420.	80.
As	26.			
B		32.	14.	23.
Ba	76.	13.	15.	29.
Be	0.66	<0.03	0.02	<0.02
Ca	17000.	18000.	3500.	7900.
Cd	2.0	<0.3	0.3	<0.2
Co	14.	0.8	0.95	0.4
Cr	12.	0.97	0.93	0.5
Cu	22.	15.	11.	7.2
Fe	13000.	300.	630.	91.
K	580.	16000.	11000.	29000.
Li	5.1	<0.3	0.3	<0.2
Mg	9000.	4600.	3100.	4000.
Mn	1100.	91.	76.	20.
Na	39.	77.	240.	92.
Ni	8.9	0.8	0.7	0.5
P	550.	1900.	2000.	1300.
Pb	120.	5.0	11.	2.
Si	27.	90.	52.	59.
Sr	8.8	18.	9.7	24.
Ti	30.	5.3	9.2	3.1
V	23.	0.6	1.2	0.3
Zn	110.	34.	14.	15.

TABLE 15 (Cont)

Element	435 Soil	435 Grass Leaves	435 Grass Stems	435 Grass Roots
Ag	<0.3	<0.4	<0.4	<0.2
Al	8600.	120.	170.	6600.
As	10.			
B		6.	<2.	11.
Ba	61.	6.1	7.0	88.
Be	0.57	<0.04	<0.04	0.73
Ca	20000.	3700.	2300.	24000.
Cd	0.8	<0.4	0.6	1.9
Co	9.2	<0.4	<0.4	13.
Cr	13.	0.9	1.9	17.
Cu	22.	6.2	5.7	25.
Fe	14000.	160.	210.	22000.
K	800.	25000.	16000.	3700.
Li	7.2	<0.4	<0.4	5.0
Mg	10000.	3800.	2500.	12000.
Mn	1000.	70.	72.	1900.
Na	62.	450.	120.	390.
Ni	8.4	1.6	2.6	6.6
P	780.	4300.	3000.	1300.
Pb	120.	5.	2.	73.
Si	100.	340.	7.	420.
Sr	11.	4.4	3.6	16.
Ti	83.	2.5	6.6	87.
V	28.	<0.4	0.5	36.
Zn	65.	25.	43.	110.

TABLE 15 (Cont)

Element	436 Soil	436 Clover Roots	436 Clover Stems	436 Clover Leaves
Ag	<0.3	<0.5	<0.3	<0.3
Al	6200.	470.	20.	67.
As	10.			
B		18.	18.	31.
Ba	58.	12.	12.	7.2
Be	0.61	<0.05	<0.02	<0.03
Ca	18000.	3500.	6600.	17000.
Cd	1.1	<0.5	<0.3	<0.3
Co	8.8	1.	<0.3	0.6
Cr	11.	1.	<0.3	1.
Cu	21.	19.	7.2	11.
Fe	13000.	720.	42.	130.
K	570.	13000.	20000.	22000.
Li	5.0	<0.5	<0.2	<0.3
Mg	9400.	4700.	3200.	3100.
Mn	1100.	110.	15.	87.
Na	46.	380.	90.	180.
Ni	7.0	5.5	<0.3	0.6
P	760.	3600.	2300.	2500.
Pb	160.	<3.	<2.	4.
Si	62.	39.	35.	82.
Sr	9.4	10.	13.	10.
Ti	34.	12.	0.3	1.
V	24.	2.	<0.2	<0.3
Zn	75.	17.	89.	37.

TABLE 15 (Cont)

Element	441 Soil	441 Grass Roots	441 Grass Leaves	441 Grass Stems
Ag	<0.3	<0.3	<0.2	<0.3
Al	9300.	3400.	180.	140.
As	17.			
B		5.	6.3	<2.
Ba	79.	220.	9.7	5.5
Be	0.65	0.68	<0.02	<0.02
Ca	10000.	11000.	5200.	1700.
Cd	1.0	0.7	0.4	0.7
Co	11.	48.	0.3	0.4
Cr	15.	12.	1.0	2.6
Cu	30.	140.	5.9	5.0
Fe	13000.	16000.	170.	260.
K	720.	4700.	29000.	24000.
Li	7.2	2.1	<0.2	<0.3
Mg	5600.	5500.	4800.	2700.
Mn	990.	3100.	92.	140.
Na	47.	600.	220.	430.
Ni	816	30.	1.1	0.9
P	690.	1400.	3400.	3900.
Pb	170	77.	7.1	<2.
Si	370.	410.	230.	4.
Sr	9.8	9.5	8.1	3.4
Ti	81.	49.	0.79	5.8
V	29.	30.	0.6	3.4
Zn	65.	120.	19.	50.

TABLE 15 (Cont)

Element	442 Soil	442 Grass Roots	442 Grass Leaves	442 Grass Stems
Ag	<0.3	<0.4	<0.3	<0.3
Al	12000.	2100.	56.	100.
As	18.			
B		6.	5.	<1.
Ba	92.	30.	8.7	9.4
Be	0.62	0.16	<0.03	<0.03
Ca	10000.	7500.	4100.	1500.
Cd	1.3	1.2	0.5	<0.3
Co	11.	4.3	<0.3	0.7
Cr	17.	4.8	0.7	0.4
Cu	16.	29.	5.3	5.1
Fe	16000.	4300.	120.	190.
K	1000.	4800.	28000.	17000.
Li	8.4	1.2	<0.3	<0.3
Mg	5700.	3400.	4400.	2100.
Mn	1000.	510.	73.	94.
Na	54.	610.	260.	170.
Ni	9.6	3.6	0.8	0.7
P	750.	1200.	3100.	2800.
Pb	84.	27.	6.4	<1.
Si	74.	500.	250.	29.
Sr	11.	7.0	7.7	3.4
Ti	130.	32.	1.	1.9
V	33.	10.	<0.3	0.5
Zn	72.	120.	18.	29.

TABLE 15 (Cont)

Element	442 Soil	442 Clover Roots	442 Clover Stems	442 Clover Leaves	442 Clover Flowers
Ag	<0.3	<0.6	<0.3	<0.3	<0.3
Al	12000.	820.	120.	30.	18.
As	18.				
B		17.	18.	18.	25.
Ba	92.	20.	24.	11.	14.
Be	0.62	0.06	<0.03	<0.03	<0.03
Ca	10000.	5600.	7800.	16000.	12000.
Cd	1.3	<0.6	<0.3	<0.3	<0.3
Co	11.	2.0	0.5	0.8	0.8
Cr	17.	2.	0.4	0.5	0.4
Cu	16.	22.	6.3	16.	13.
Fe	16000.	1900.	170.	110.	78.
K	1000.	10000.	24000.	22000.	19000.
Li	8.4	<0.6	<0.3	<0.3	<0.3
Mg	5700.	4100.	2400.	3500.	3700.
Mn	1000.	200.	34.	89.	58.
Na	54.	620.	120.	250.	110.
Ni	9.6	1.8	0.4	1.2	0.8
P	750.	2300.	1400.	1600.	3100.
Pb	84.	6.9	2.	10.	4.2
Si	74.	250.	3.	89.	83.
Sr	11.	12.	19.	14.	17.
Ti	130.	12.	2.5	<0.3	<0.3
V	33.	3.9	0.3	<0.3	<0.3
Zn	72.	18.	16.	40.	30.

TABLE 16

SOIL ANALYSIS (AAS) FOR SAMPLE SITES ON FERGUSON FARM

Sample No.	Metal Conc; ug/g			
	Pb	Cd	Zn	Cu
422	20	<.3	38	8
423	20	<.3	31	8.2
424	20	<.3	21	6.1
427	130	<.3	22	4.3
428	40	<.3	24	6.1
429	20	<.3	25	7.0
432	20	<.3	21	5.1
433	200	<.3	72	32
434	200	<.3	25	38
438	82	<.3	64	59
439	80	<.3	34	17
440	110	<.3	37	16
443	30	<.3	31	11
444	30	<.3	24	10
445	30	<.3	22	9
446	41	<.3	26	-
447	220	<.3	94	-
448	200	<.3	69	-

A second location where tailings material had been used for agricultural limestone purposes was suggested by Mr. Burton L. Brown of the U. S. Soil Conservation Service in Farmington, Missouri. This pasture was approximately one mile south of Farmington, Missouri and named "Young Farmers" after the cooperative association that owned the land. Soil and grass samples were taken from this area and the analytical findings (ICAP) are presented in Table 17. The soil samples indicated 180 μg/g Pb while the grass roots from the same soil contained 6 μg/g Pb and the leaves contained 9 μg/g Pb.

A normal Crider soil was suggested by Mr. Burton using his soil report (19) to locate a typical control soil and the ICAP analysis for this soil taken from an undeveloped field one mile north of Farmington, Missouri is shown in Table 18. Interestingly enough, the undisturbed control soil was found to contain 140 μg/g Pb and the grass growing in this material contained 9 μg/g Pb in the roots and 6 μg/g Pb in the blades again indicating that the Pb is not bioconcentrated in the plant from the soil material. Leaf litter at the control soil area was analyzed to determine if atmospheric fallout might influence the metal levels and the levels were found not to be of concern (Table 18).

The Crider soil selected for the natural control soil was also used in the experimental plant growth experiments conducted in the laboratory.

TABLE 17

SOIL AND VEGETATION ANALYSIS (ICAP) FOR THE YOUNG FARMERS FIELD WHERE TAILINGS WERE USED FOR AGRICULTURAL LIMESTONE (UNITS IN MICROGRAMS/GRAM)

Element	YF-1 Soil	YF-1 Grass	YF-1 Roots
Ag	< 1.	5.7	2.4
Al	6100.	260.	530.
B	20.	4.	10.
Ba	140.	29.	14.
Be	0.51	< 0.1	< 0.1
Ca	3700.	3600.	1500.
Cd	0.5	< 0.6	< 0.5
Co	8.4	< 0.6	< 0.5
Cr	15.	< 0.6	< 0.5
Cu	13.	8.7	11.
Fe	10000.	260.	410.
K	680.	16000.	6300.
Li	4.0	< 0.6	< 0.5
Mg	1800.	2200.	700.
Mn	1300.	83.	63.
Na	25.	130.	180.
Ni	9.4	4.8	0.8
P	540.	2900.	1700.
Pb	180.	9.	6.
Si	120.	380.	210.
Sr	6.5	6.0	2.5
Ti	56.	8.4	23.
V	20.	0.8	1.7
Zn	65.	42.	47.

TABLE 18

SOIL AND VEGETATION ANALYSIS (ICAP) FOR
CRIDER SOIL (CONTROL) NEAR FARMINGTON, MISSOURI
(UNITS ARE IN MICROGRAMS/GRAM)

Element	C-11 Soil	C-11 Roots	C-11 Stems	C-11 Leaves
Ag	< 0.3	< 0.6	< 0.5	< 0.6
Al	11000.	3100.	590.	350.
B	6.	16.	3.	3.
Ba	230.	89.	73.	42.
Be	0.70	< 0.1	< 0.1	< 0.1
Ca	1600.	3100.	3400.	1900.
Cd	< 0.3	< 0.6	< 0.5	< 0.6
Co	12.	3.2	1.	< 0.6
Cr	22.	2.0	< 0.5	< 0.6
Cu	9.5	15.	6.4	9.7
Fe	13000.	2200.	480.	310.
K	1400.	19000.	9700.	43000.
Li	7.7	1.9	< 0.5	< 0.6
Mg	1200.	1800.	1700.	1900.
Mn	1700.	520.	430.	220.
Na	27.	330.	200.	47.
Ni	14.	4.1	0.6	3.0
P	300.	1200.	590.	2500.
Pb	140.	7.	9.	< 6.
Si	200.	1900.	150.	77.
Sr	11.	17.	16.	8.7
Ti	170.	150.	22.	12.
V	30.	7.7	1.6	0.9
Zn	37.	50.	31.	26.

VII. COMMERCIAL LIMESTONE STUDY

It was necessary to determine the elements present in commercial agricultural limestone which was used as a control during the experimental growth studies. Mr. Paul R. Rexroad and Ms. Mary A. Pagett at the Agriculture Experiment Station Chemistry Lab of the University of Missouri-Columbia were kind enough to furnish information on the list of lime quarries and stockpiles by counties. After further consultation, thirteen samples were selected for ICAP analysis at the ETSRC in Columbia to determine baseline elemental composition.

Four samples were selected from neighboring states (Illinois, Iowa, Arkansas and Kansas) and the remainder of the samples were from within the State of Missouri. Three of the samples selected for comparison in the State of Missouri were from old lead belt mining operations.

Table 19 indicates the identification number, name and location of the limestone quarry followed by the identification number used by the ETSRC for the ICAP analysis. Table 20 presents the ICAP data for the various commercial agricultural limestone used in this study.

TABLE 19

LOCATION OF COMMERCIAL AGRICULTURAL LIMESTONE
USED IN STUDY AND LEAD CONTENTS (ug/g)

Customer I.D.	Quarry	Location	Sample #	Pb (ug/g)
2039	Calcium Carbonate Co.	Quincy, Illinois	83010076	9.
2011	Ampel	Des Moines, Iowa	77	8.
1976	Twin Lakes	Midway, Arkansas	78	12.
2006	Cullor L.S. Co.	Ft. Scott, Kansas	79	11.
2088	Conco Quarries	Springfield, Mo.	80	11.
1918 (2)	St. Joe Minerals Corp.	Viburnum, Mo. **	81	350.
2019	Rolla Materials, Inc.	Rolla, Mo.	82	8.
2025	Jeff-Cole Co.	Jefferson City, Mo.	83	8.
1919 (1)	Agric Limestone Co.	Bonne Terre, Mo. *	84	1800.
1921 (1)	James D. Allen Materials	Farmington, Mo. *	85	1700.
1922 (1)	Lead Belt Materials Co., Inc.	Flat River, Mo. *	86	1100.
1949	Mississippi Lime Co.	Ste. Genevieve, Mo.	88	13.
1993	Harris Lime	Patterson, Mo.	89	7.

* Denotes Old Lead Belt Area
** Denotes New Lead Belt Area

TABLE 20

ICAP ANALYSIS (ug/g) FOR COMMERCIAL LIMESTONE

	2039 83010076	2011 83010077	1976 83010078	2006 83010079
Ag	< 7.	< 7.	< 7.	< 7.
Al	< 50.	400.	920.	1800.
As	< 70.	< 70.	< 70.	< 70.
B	< 30.	< 30.	< 30.	< 30.
Ba	2.	8.0	2.	16.
Be	< 1.	< 1.	< 1.	< 1.
Ca	367000.	251000.	171000.	334000.
Cd	< 7.	< 7.	< 7.	< 7.
Co	< 7.	< 7.	< 7.	< 7.
Cr	< 7.	21.	15.	< 7.
Cu	< 7.	< 7.	29.	16.
Fe	390.	1900.	3300.	5400.
K	< 500.	< 500.	< 500.	< 500.
Li	< 7.	< 7.	< 7.	< 7.
Mg	3300.	70000.	98000.	4400.
Mn	220.	210.	120.	420.
Na	200.	330.	150.	92.
Ni	< 7.	14.	10.	13.
P	< 70.	3400.	350.	360.
Pb	< 30.	< 30.	< 30.	< 30.
Se	< 70.	< 70.	< 70.	< 70.
Si	100.	430.	340.	260.
Sn	< 70.	< 70.	< 70.	< 70.
Sr	96.	180.	72.	970.
Ti	< 10.	< 10.	< 10.	< 10.
V	< 7.	< 7.	< 7.	8.
Zn	110.	36.	340.	81.

TABLE 20 (Cont)

ICAP ANALYSIS (ug/g) FOR COMMERCIAL LIMESTONE

As	2088 83010080	1918(2) 83010081	2019(1) 83010082	2025 83010083
Al				
As	< 7.	< 7.	< 7.	< 7.
B	300.	60.	750.	1200.
Ba	< 70.	< 70.	< 70.	< 70.
Be	< 30.	< 30.	< 30.	< 30.
Ca	2.	3.6	7.0	4.5
Cd	< 1.	< 1.	< 1.	< 1.
Co	365000.	191000.	163000.	155000.
Cr	< 7.	10.	< 7.	< 7.
Cu	< 7.	19.	< 7.	< 7.
Fe	< 7.	< 7.	10.	11.
K	12.	290.	15.	19.
Li	490.	12000.	4400.	2900.
Mg	< 500.	< 500.	< 500.	< 500.
Mn	< 7.	< 7.	< 7.	< 7.
Na	1400.	110000.	94000.	91000.
Ni	200.	1700.	180.	180.
P	180.	170.	180.	160.
Pb	< 7.	33.	10.	11.
Se	100.	300.	1100.	620.
Si	< 30.	340.	< 30.	< 30.
Sn	< 70.	< 70.	< 70.	< 70.
Sr	160.	280.	240.	230.
Ti	< 70.	< 70.	< 70.	< 70.
V	150.	54.	59.	59.
Zn	< 10.	< 10.	< 10.	< 10.
	< 7.	< 7.	7.	< 7.
	16.	750.	7.	< 7.

TABLE 20 (Cont)

ICAP ANALYSIS (ug/g) FOR COMMERCIAL LIMESTONE

	1919(1) 83010084	1921(1) 83010085	1922(1) 83010086	1949 83010088	1993 83010089
Ag	< 7.	< 7.	< 7.	< 7.	< 7.
Al	140.	150.	300.	80.	880.
As	< 70.	< 70.	< 70.	< 70.	< 70.
B	60.	40.	< 30.	< 30.	< 30.
a	11.	3.9	3.	8.7	8.0
Be	< 1.	< 1.	< 1.	< 1.	< 1.
Ca	192000.	184000.	189000.	371000.	196000.
Cd	< 7.	24.	42.	< 7.	< 7.
Co	27.	15.	20.	< 7.	< 7.
Cr	7.	8.	11.	14.	< 7.
Cu	170.	93.	40.	8.	20
Fe	44000.	31000.	22000.	360.	2900.
K	< 500.	< 500.	< 500.	< 500.	< 500.
Li	< 7.	< 7.	< 7.	< 7.	< 7.
Mg	91000.	92000.	102000.	1800.	115000.
Mn	5300.	4500.	3500.	16.	140.
Na	230.	260.	230.	110.	260.
Ni	28.	17.	24.	< 7.	< 7.
P	310.	430.	320.	80.	300.
Pb	1700.	1600.	1100.	< 30.	< 30.
Se	< 70.	< 70.	< 70.	< 70.	< 70.
Si	270.	280.	310.	120.	260.
Sn	< 70.	< 70.	< 70.	< 70.	< 70.
Sr	36.	44.	47.	140.	53.
Ti	< 10.	< 10.	< 10.	< 10.	< 10.
V	10.	7.	7.	< 7.	8.
Zn	350.	860.	2100.	32.	22.

VIII. PLANT METAL UPTAKE STUDIES

Using the survey of metal contents in tailings and chat piles from the Old Lead Belt of Missouri with high lead values, bulk samples were then collected from areas with the highest known lead content for use as limestone in laboratory plant growth experiments. Quantities of tailings material from the New Lead Belt mill operations were also collected for comparison. The tailings were analyzed for cadmium and lead prior to experimental soil preparation.

The experimental design involved the mixing of tailings with an uncontaminated acid soil derived from the Old Lead Belt area. The typical soil chosen belongs to the Crider series. This is a dark brown silt loam formed in loess or clay residuum with pH in the top 20 cm being approximately 5.0 unless limed. The soil is classified as a mesic Typic Paleudalf (19).

In a control study, the same acid soil was amended with equivalent amounts of a commercial agricultural limestone, known to contain only background levels of heavy metals. For further comparison, soil was collected from a farm where Old Lead Belt tailings had been spread on the land over a number of years.

Soil samples were laid out on polyethylene sheeting to dry in the laboratory. Large particles and stones were removed by hand. Dried soils were ground with a large mortar and pestle and passed through a stainless steel sieve of 2 mm aperature. The sieved material was then mixed with coarse gravel (inert) at a ratio of 3:1 to improve drainage. The experimental soil mixtures used for plant growth were prepared by mixing the appropriate soil sample with commercial agricultural limestone or tailings on a volume basis.

The various types of soils and amended soils utilized for laboratory plant growth experiments were as follow:

1. Uncontaminated control soil (Crider)
2. Control soil:commercial agricultural limestone (3:1)
3. Control soil:commercial agricultural limestone (7:1)
4. Control soil:New Lead Belt tailings (3:1)
5. Control soil:New Lead Belt tailings (7:1)
6. Control soil:Old Lead Belt tailings (3:1)
7. Control soil:Old Lead Belt tailings (7:1)
8. Ferguson Farm soil (previously treated with Old Lead Belt tailings as agricultural limestone)

Each of these soil mixtures was used to prepare six experimental pots. Each pot received a bottom layer of glass fiber, 2.5 cm thick over which the soil mixture was placed. Prior to planting, each pot received a surface application of liquid fertilizer and was allowed to equilibrate for 48 hours.

Radish (French Breakfast) and lettuce (Paris White) seeds were sown at a rate of 25 per pot and covered with a 1 cm layer of the appropriately treated soil. All pots were placed in a commercial greenhouse in a randomised block, and watered thoroughly from below with local tapwater.

Initial growth was rapid and the plants were thinned to 10 per pot for radish and 5 per pot for lettuce. Plants were harvested after 6 weeks.

At harvest, plants were divided into leaves and roots, and tubers in the case of radish. Each plant part was weighed, washed thoroughly with distilled water to remove soil particles, and dried in paper bags for 24 hours in an oven with a forced draught and set at 90 C. After drying, plants were reweighed, ground and sent to the Environmental Trace Substances Laboratory at Columbia, Missouri, for analysis. Soil samples from each pot were also collected and analysed. Analysis was by the inductively coupled argon plasma emission method, or flameless atomic absorption for lead.

RESULTS AND DISCUSSION

The analytical values for the soils and limestones are illustrated in Table 21.

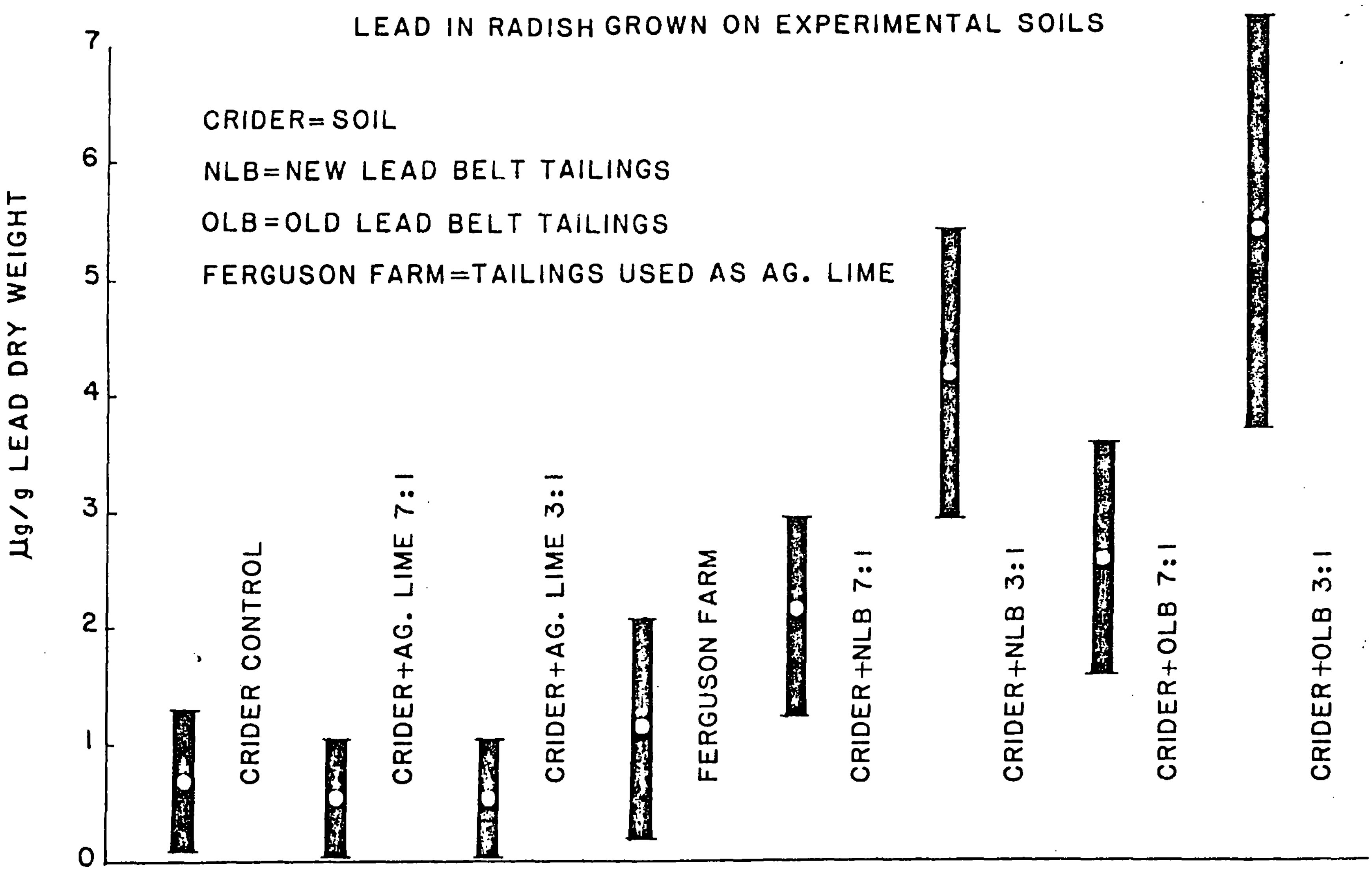
For each treatment, the mean and standard error of the three replications of each plant was calculated on a dry weight basis. These are presented graphically for Pb and Cd in radish bulbs in Figures 13 and 14. Figures 15 and 16 illustrate the Pb and Cd in lettuce leaves. For each diagram the treatments have been ranked in order of increasing metal contents of the treatments left to right along the X axis.

The diagrams for lead indicate a distinct upward trend in metal content of plants from left to right, i.e. as soil metal levels increase. The trend for Cd is not as marked.

The highest levels of Pb in the soils were noted in the 3:1 mixtures of Old Lead Belt tailings and these soils yielded radish with the highest Pb contents, in the range 5 - 7 μg/g dry matter. One way of interpreting these values is to use the maximum permissible limit for lead in food in Great Britain. In Britain it is an offense to sell food containing >1μg Pb/g on a fresh weight basis. Although the

TABLE 21
LEAD, CADMIUM AND ZINC IN
SOIL, TAILINGS AND AGRICULTURAL
LIME USED IN EXPERIMENTAL SOILS
(MICROGRAMS/GRAM DRY WEIGHT)

	CRIDER (SOIL CONTROL)	AG LIME (STE. GENEVIEVE)	FERGUSON FARM	NEW LEAD BELT TAILINGS	OLD LEAD BELT TAILINGS
PB	29	7.3	41	320	9100
CD	< 0.3	< 0.3	< 0.3	7.5	64
ZN	35	21	26	500	3100



LEAD IN RADISH GROWN ON EXPERIMENTAL SOILS
CRIDER= SOIL
NLB=NEW LEAD BELT TAILINGS
OLB=OLD LEAD BELT TAILINGS
FERGUSON FARM=TAILINGS USED AS AG. LIME
μg/g LEAD DRY WEIGHT
0
1
2
3
4
5
6
7
CRIDER CONTROL
CRIDER+AG. LIME 7:1
CRIDER+AG. LIME 3:1
FERGUSON FARM
CRIDER+NLB 7:1
CRIDER+NLB 3:1
CRIDER+OLB 7:1
CRIDER+OLB 3:1

FIGURE 13.

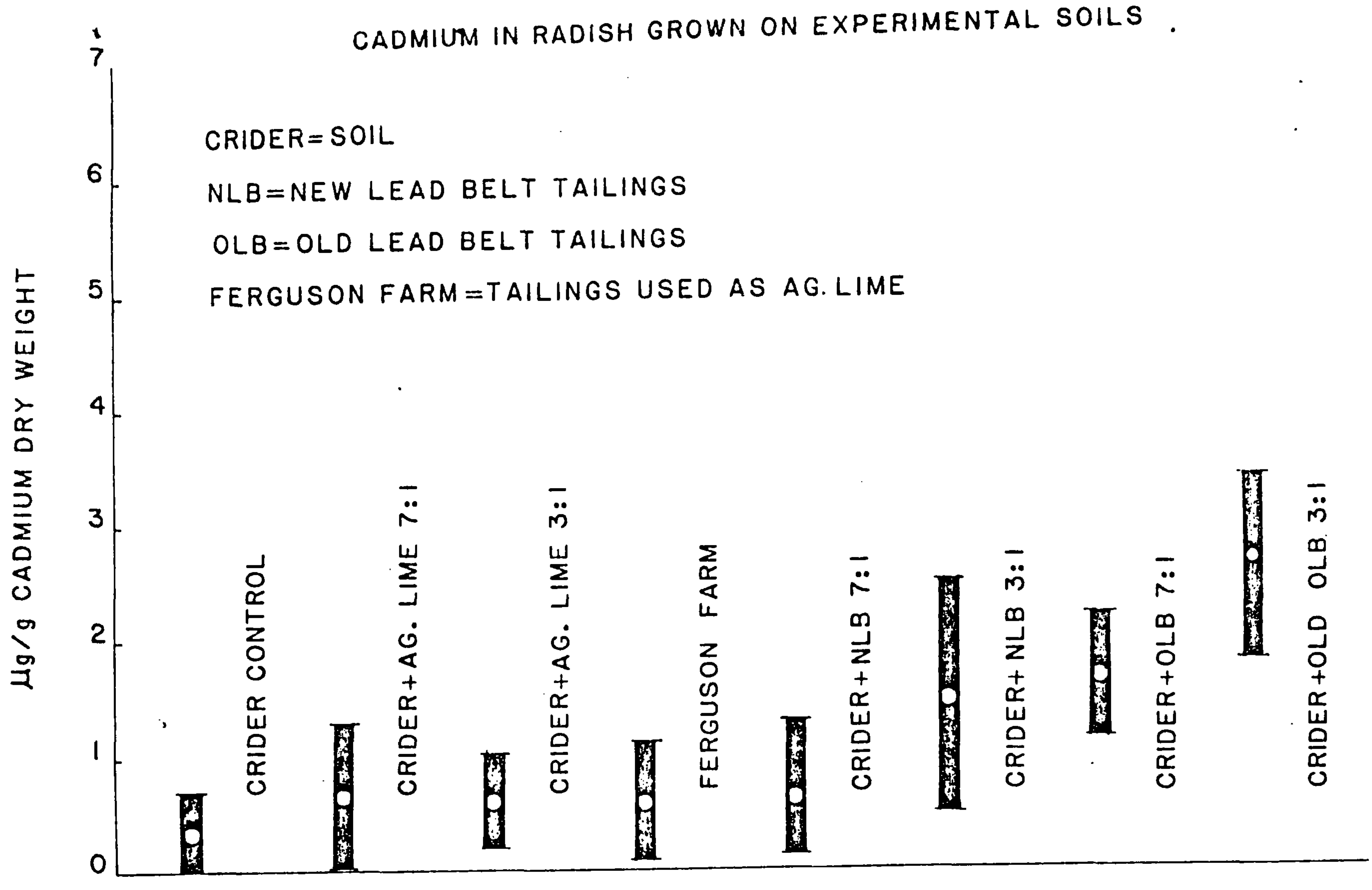

CADMIUM IN RADISH GROWN ON EXPERIMENTAL SOILS
CRIDER=SOIL
NLB=NEW LEAD BELT TAILINGS
OLB=OLD LEAD BELT TAILINGS
FERGUSON FARM=TAILINGS USED AS AG. LIME
μg/g CADMIUM DRY WEIGHT
0
1
2
3
4
5
6
7
CRIDER CONTROL
CRIDER+AG. LIME 7:1
CRIDER+AG. LIME 3:1
FERGUSON FARM
CRIDER+NLB 7:1
CRIDER+NLB 3:1
CRIDER+OLB 7:1
CRIDER+OLD OLB 3:1

FIGURE 14.

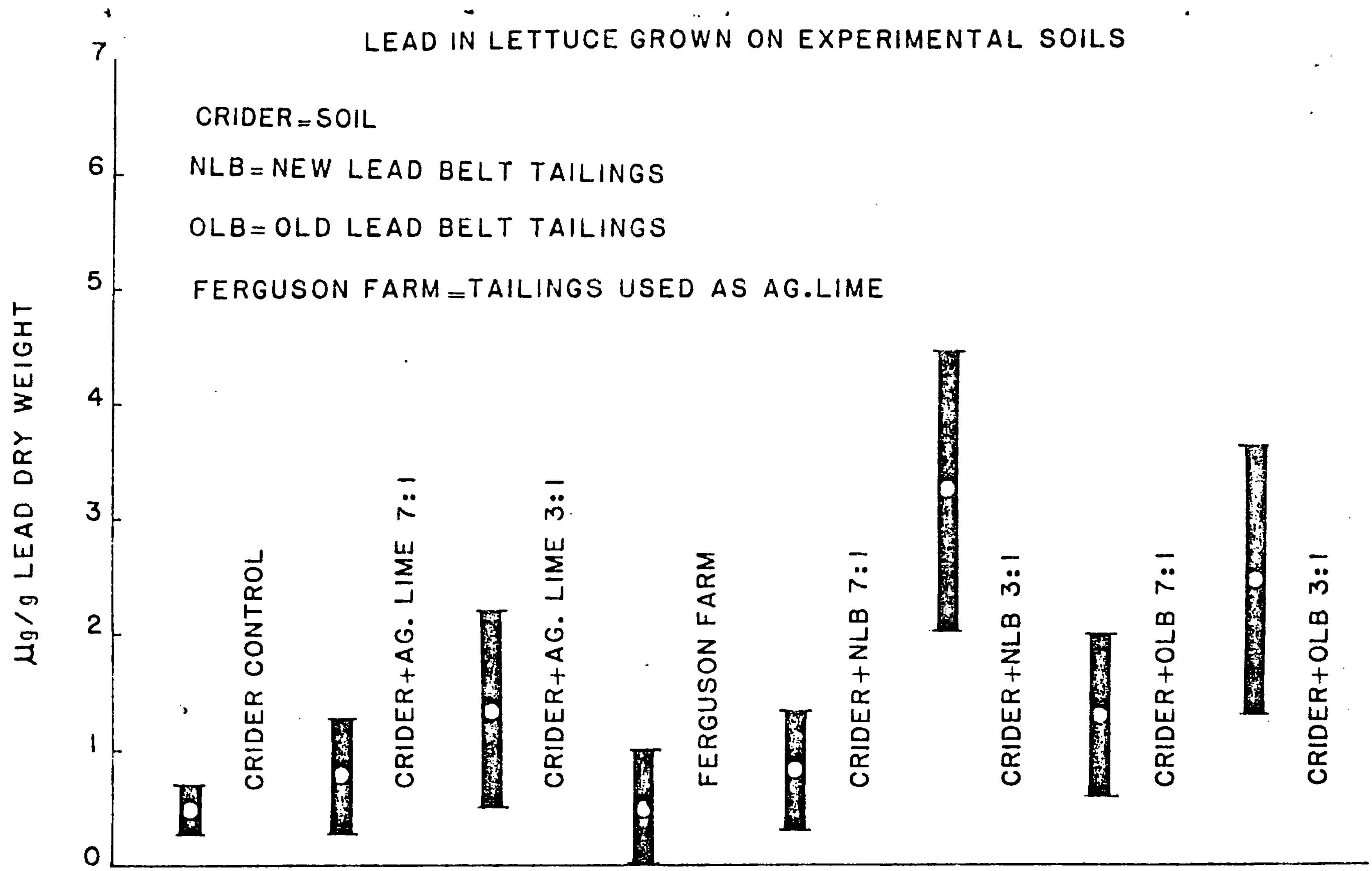

LEAD IN LETTUCE GROWN ON EXPERIMENTAL SOILS
CRIDER = SOIL
NLB = NEW LEAD BELT TAILINGS
OLB = OLD LEAD BELT TAILINGS
FERGUSON FARM = TAILINGS USED AS AG.LIME
μg/g LEAD DRY WEIGHT
0
1
2
3
4
5
6
7
CRIDER CONTROL
CRIDER+AG. LIME 7:1
CRIDER+AG. LIME 3:1
FERGUSON FARM
CRIDER+NLB 7:1
CRIDER+NLB 3:1
CRIDER+OLB 7:1
CRIDER+OLB 3:1

Figure 15.

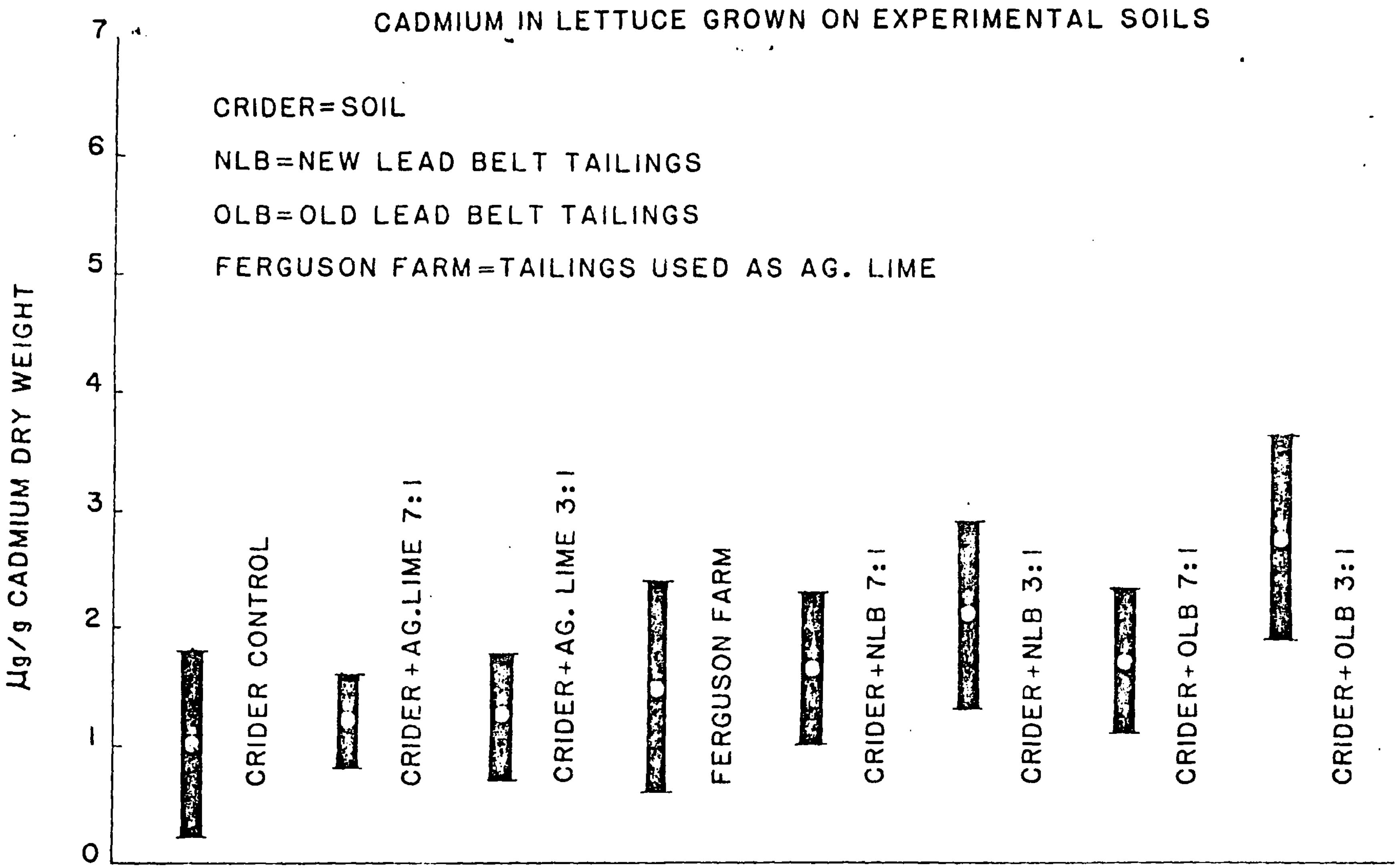

CADMIUM IN LETTUCE GROWN ON EXPERIMENTAL SOILS
CRIDER=SOIL
NLB=NEW LEAD BELT TAILINGS
OLB=OLD LEAD BELT TAILINGS
FERGUSON FARM=TAILINGS USED AS AG. LIME
μg/g CADMIUM DRY WEIGHT
0
1
2
3
4
5
6
7
CRIDER CONTROL
CRIDER+AG.LIME 7:1
CRIDER+AG. LIME 3:1
FERGUSON FARM
CRIDER+NLB 7:1
CRIDER+NLB 3:1
CRIDER+OLB 7:1
CRIDER+OLB 3:1

FIGURE 16

dry matter content of vegetables is variable it is a useful approximation to suppose most contain about 10% dry matter and the permissible limit therefore converts to 10 μg/g dry weight. The highest lead contents of the radish are lower than this limit. Levels in the lettuce are even lower and lettuce dry matter contents are more usually nearer 5% than 10%. It is interesting to note that in both lettuce and radish, slightly elevated levels occurred in the New Lead Belt 3:1 tailings. This suggests that even though the New Lead Belt tailings contain less Pb than the Old Lead Belt ones, when added at a rate of 3:1 (soil:tailings), soil Pb levels could become higher than those observed when Old Lead Belt tailings are added at a rate of 7:1 (soil:tailings). In the case of lettuce, New Lead Belt tailings at 3:1 produced higher plant levels than Old Lead Belt tailings at 3:1.

The Cd contents of radish and lettuce showed a similar trend to that of Pb, i.e., increasing with the content of the underlying soil. Levels in the highest Cd treatment were 6 times those in the control for radish and 3 times those for lettuce, and in both cases this was about 3 μg/g dry weight. On a fresh weight basis, this would correspond to 0.3 μg/g for radish and 0.15 μg/g for lettuce. In neither Great Britain nor the USA is the food content of cadmium controlled by law. Davies and White (20) argued that, using the same premises that were used to derive a lead limit, a limit of 0.2 μg Cd/g wet weight is applicable. The highest radish value is above the limit of 0.2 mg/kg for Cd suggested by Davies and White (20).

The liming regimes used in this experiment were far in excess of those which would be considered normal agricultural practice. In normal liming practices, two tons of lime are applied to one acre of soil (top 6 inches). Using calculations for Crider soil, this represents two tons of agricultural lime per 1089 tons of soil or a ratio of 544:1 (soil-to-lime). Hence with normal rates of application, metal levels accumulated by crops would be expected to be far lower. This was in fact observed where the plants were grown on the Ferguson farm soil which has received mill tailings as agricultural limestone over a number of years. However, the low uptake observed could also be a function of the high pH maintained by the added lime. In practice therefore, uptake may increase if high metal levels are allowed to accumulate in soils, and are subsequently made more available by a lowering of pH e.g. by discontinuation of the liming regime.

IX. CONCLUSIONS

Five of the major chat or tailings piles and areas in the "Old Lead Belt" of Missouri have been sampled, analyzed and evaluated for the concentrations and distributions of pertinent metals. Near surface and core samples were collected in sufficient numbers and patterns to statistically characterize the studied deposits resulting from different separation techniques employing jigging or froth flotation technology.

The National and Elvins tailings piles were found to contain the highest mean Pb values (4000-6800 ppm) while the Leadwood deposit contained the highest mean Cd values (267 ppm) coupled with elevated zinc concentrations (5482 ppm). Each tailings or chat pile and area displayed specific characteristics that may be utilized in planning for stabilization, revegetation, control of runoff discharges into streams or rivers determining impacts on biota, or utilization of these waste rock materials for construction, agricultural limestone or other constructive uses.

Field studies carried out in pastures where tailings from the "Old Lead Belt" had been used for a number of years as agricultural limestone did not indicate any significant movement of Pb, Cd, or Zn from the tailings enriched soil into the roots, stems or leaves of the grass or clover analyzed. Control soil and vegetation growing in the same samples indicated a similar trend of no bioconcentration of elements from the soil.

A number of commercial limestone samples from Missouri and from neighboring states were analyzed for comparison with tailings and local limestone used in laboratory plant growth and bioassay experiments to ascertain whether the Old and/or New Lead Belt tailings could be used as agricultural limestone without elevating heavy metal contents of farm crops to unacceptable levels.

Plant metal uptake studies indicated that both lettuce and radish tended to accumulate some of the Pb and Cd added when lead-zinc mill tailings were mixed with soil as agricultural limestone. Radish bulbs accumulated Pb to a higher degree than lettuce, but both accumulate Cd to the same level. However, neither was considered a health hazard according to accepted or proposed standards for Cd and Pb in food with the possible exception of radish grown at the highest rate of appliction of Old Lead Belt tailings, which is significantly higher than normal liming practices.

This research evaluation of the data suggests that dolomitic limestone tailings in Southeast Missouri from both the Old and New Lead Belts could be used as a cheap and convenient substitute for agricultural limestone with resultant environmental benefits (21). Utilization of tailings on a broader scale would also enable much of the chat or tailings piles to be removed as a resource material and thereby eliminate some of the stability and erosion problems while improving the appearance of the landscape. However, since the different milling waste piles contain varying amounts of cadmium and lead, the materials selected for such use should not contain elevated metal levels found in some of the older chat or tailings locations characterized in this study.

ACKNOWLEDGEMENTS

Many different people, agencies or industries have participated or helped with this study and the authors would like to acknowledge their efforts.

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John Carter, St. Joe Minerals Corporation was most helpful in assisting with field work and admission to St. Joe property and data. Special thanks must go to Theodore Ferguson and his family for allowing us to sample his farm pasture. Burton Brown from the soil conservation service in Farmington, Missouri gave of his time, shared data and suggested area soils for the study.

Mr. Lee Cash of the Lead Belt Materials Company and Gayle Blackwell and George Carroul of the St. Francis County Environmental Corporation allowed our team to sample on their properties.

Larry George, Glynn Horter and Scot Lay from the Bureau of Mines in Rolla, Missouri assisted with auger and coring work on the tailings piles. The permission to include the Bureau data and assistance of Don Paulson is also appreciated.

Paul Rexroad and Mary Pagett at the University of Missouri-Columbia helped with the selection of commercial limestone for analysis. The analytical preparation and analysis carried out by Ed Hindergerger, Millie Kaiser and Tom Clevenger at the Environmental Trace Substances Research Center in Columbia, Missouri gave the quality control needed for the study.

Heyward Wharton from the Missouri DNR Division of Geology and Land Survey furnished maps, suggestions and data that were most helpful. Dr. Brian Davies was a visiting professor at the University of Missouri-Rolla during this research and thanks to UMR and the University College of Wales-Aberystwyth, Wales for their support.

Larry Elliott completed his M.S. Thesis on the National Tailings pile with support from the Missouri DNR.

Special thanks must go to the students and staff associates who sweated long hours in the sun or lab to collect the necessary samples and data. They are Bill Ray, Tanzeer Ahmed, Nicola Houghton, David Schlotzhauer, Ross Hazelhorst and Sue Hills.

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APPENDIX

United States Department of the Interior
BUREAU OF MINES
1300 BISHOP AVENUE
ROLLA, MISSOURI 65401

October 28, 1983

Dr. Bobby G. Wixson
Professor of Environmental Health
University of Missouri - Rolla
321 Engineering Research Lab
Rolla, Mo. 65401

OCT 31.

Dear Dr. Wixson:

Thank you for your recent letter acknowledging the cooperation provided by Bureau of Mines employees at the Rolla Research Center. We are pleased that their assistance was beneficial, especially the supplemental data that you wish to include in your final report on the characterization of the lead tailings piles in southeast Missouri.

The analytical results and other technical assistance that was provided by the Bureau may be incorporated in your final report.

If we can be of further assistance in the future, please let us know.

Sincerely yours,

D. L. Paulson
Research Director
Rolla Research Center

MISSOURI DEPARTMENT OF NATURAL RESOURCES
P.O. Box 1368   2010 Missouri Blvd.   Jefferson City, Missouri 65102   (314) 751-3241

October 6, 1981

Dr. Bobby Wixson
University of Missouri, Rolla
Rolla, Missouri 65401

Dear Dr. Wixson:

Thank you for forwarding copies of the preliminary data from the sampling and analysis of heavy metals in selected chat piles and tailings ponds. There were several interesting points including:

1. The great variability in zinc concentration between chat piles.

2. The apparent "enrichment" of material at the outflow from the Flat River pile which suggests some selective process.

I have put together some comments on the variances of the samples you have taken and how they relate to adequate sample size (no. of samples). It appears that with the number of samples taken the sample means for metals levels in chat piles are within 30% of the true mean, and in the Desloge tailings within 15% of the true mean. These figures assume a 95% confidence level.

I would welcome your comments on the attached materials which document my estimation of appropriate sample sizes.

Sincerely,

John C. Ford
Environmental Specialist
Water Pollution Control Program

JCF:jc

I believe there are 2 types of conclusions concerning heavy metals concentrations in tailings that require some degree of statistical corroboration.

1. The mean or average concentration of a given metal in a particular chat pile or tailings pond, and
2. The mean concentration of a given metal in one chat pile or tailings pond relative to the mean concentration of that metal in a second chat pile or tailings pond.

The following procedure is my attempt to calculate the minimum sample size necessary to provide that statistical cooroboration.

In order to make estimates of a certain precision that are representative of a population at a given level of confidence, the following formula is used.

$$n = \frac{t^2 s^2}{d^2}$$

Where
n = no. of samples
t = Student's t (confidence level desired)
s^2 = population variance estimate
d = desired precision

Student's t

I wish to use a 95% confidence level. Assuming cost restraints will put the sample size in the range of $3 \leq n \leq 15$, then $2.35 < t < 1.75$. For the purposes of estimating sample size (which must be rounded off to a whole number, anyway) I will use t = 2.

Population Variance Estimate, s^2

I made four separate estimates of population variance for Pb, Zn and Cd. In choosing samples, I was careful not to include samples sites that may have been of different origin. Thus, at the Elvins chat pile, the coarse material (sample 87) was not included nor were tailings moved by water (samples 76-80.) At the Flat River pile, the material in the lower pile (samples 55-57) were not included.

Results are as follows based upon metals concentration in parts per million.

		Approx. Sample Variance (s^2)		
Location	Sample Numbers	Pb	Zn	Cd
Elvins Chat Pile	73-75, 81-84	623,000	2,400,000	687
Flat R. " "	49-54, 58,59,63,64	3,250,000	13,800	7.6
Leadwood" "	36-38, 42-47	3,000,000	9,000,000	3,086
Deslodge Tailings Pond	24-30	160,000	54,000	35.3

The high variance for Zn at Leadwood is caused by 2 of the nine values. If we consider them outliers and ignore them for the moment, then the maximum variance we are experiencing at the 3 chat piles is about 3 million and for the tailings pond, 160,000.

Desired Precision, d.

Precision here is the maximum allowable difference between the sample estimate and the true population valve which can be detected with a given level of confidence. In this case, I have chosen one-tenth of the sample mean. Asking for considerably more precision than this, like .01 of the sample mean may be exceeding the capability of the analytical procedures.

For simplicity, an average value of d for chat piles of 300 was used for Pb and 400 for Zn (a value of 25.7 will be used for the Flat River pile since it is considerably different in /Zn/.

	Value of d		
Location	Pb	Zn	Cd
Elvins Chat Pile	260	377	7.3
Flat R. " "	408	25.7	5.4
Leadwood" "	295	463	9.1
Desloge Tailings Pond	176	126	2.7

Calculation of Sample Size, n

		t^2	s^2	d^2	n
Chat Piles	Pb	4	3.10^6	90,000	133
	Zn	4	3.10^6	160,000	75
Flat R. Zinc	Zn	4	13,800	660	84
	Cd	4	3,000	50	240
Tailings Ponds	Pb	4	160,000	31,000	21
	Zn	4	54,000	16,000	14
	Cd	4	35.3	7	20

The high variances in Pb, Zn and Cd concentrations in chat result in the large number of samples required to obtain a sample estimate within 10% of the true mean, 95% of the time. By looking at the log of the metals concentrations, sample variances can often be reduced.

Transformation of Data

All metals concentrations were transformed as follows ($\log_{10}$ concentration) +1.

This leads to the following set of sample variances.

	$\hat{s}^2$		
Location	Pb	Zn	cd
Elvins Chat Pile	.019	.037	.025
Flat R. Chat Pile	.030	.056	.052
Leadwood Chat Pile	.050	.059	.054
Desloge Tailings Pond	.011	.007	.009

"d" transformed becomes $\left[(\log_{10} \text{sample mean}) + 1\right] - \left[\log_{10} .9 \text{ sample mean}) + 1\right]$

	"d"		
Location	Pb	Zn	cd
Elvins/Leadwood Chat	0.05	0.04	0.05
Flat R. Chat Pile	0.05	0.05	0.05
Desloge Tailings	0.05	0.05	0.05

Location		t^2	s^2	d^2	n
Elvins/Leadwood Chat	Pb	4	.050	.0025	80
	Zn	4	.059	.0016	148
	Cd	4	.054	.0025	86
Flat R. Chat	Zn	4	.056	.0025	90
Desloge Tailings	Pb	4	.011	.0025	18
	Zn	4	.007	.0025	11
	Cd	4	.009	.0025	14

By reducing the amount of precision, smaller sample numbers are obtained. They are summarized as follows:

			Sample mean and true mean within		
Location	Material	Metal	10% for log	15% transformed data	20%
Elvins/Leadwood	Chat	Pb	80	41	20
		Zn	148	48	29
		Cd	86	44	22
Flat R.	Chat	Pb	80	41	20
		Zn	90	46	22
		Cd	86	44	22
Desloge	Tailings	Pb	18	9	4
		Zn	11	6	3
		Cd	14	7	4

2. Choosing sample size to determine relative concentrations in 2 or more piles requires hypothesis testing. Tables are available to give number of samples needed once the following variables are estimated or defined.

δ - the difference between means which will be detected —— percent of the time when a true difference exists.

σ - an estimate of population standard deviation

α - the probability of saying a true difference exists when the samples are really from the same population.

$(1-\beta)$ - the probability that the test detects a true difference when a true difference actually exists.

δ:

We will use the same values for δ that we did for "d" for the transformed data.

σ:

We will use the standard deviations of the samples. $\alpha, (1-\beta)$: We will define $\alpha = .05$ and $(1-\beta) = .80$

Using the attached table the appropriate sample sizes are:

Sample size n (for each of Z samples)

		δ = .05	δ = .07	δ = .10
Elvins/Leadwood Chat Piles	Pb	> 100	> 100	83
	Zn	> 100	> 100	>100
	Cd	>100	>100	90
Flat R. Chat Pile	Pb	>100	>100	83
	Zn	>100	> 100	95
	Cd	>100	>100	90
Desloge Tailings Pond	Pb	75	37	19
	Zn	45	24	12
	Cd	60	32	16

Conclusions

The high variability of metals concentrations in chat mean that large numbers of samples will be needed to make conclusions with a high level of confidence. It will take between 20-25 samples to come within 20% of the true mean metals content of a chat pile, 40-50 samples to come within 15% and 80-100 samples to come within 10% of the true mean metal content. Log transformation has been used and has resulted in a slight decrease in necessary samples size.

Tailings, which are typically more homogeneous do not require as many samples. Only 10-20 samples are required to achieve a sample mean within 10% of the true mean, and only 4 samples to have a sample mean within 20% of the true mean.

Hypothesis testing which would determine which of two sets of materials contained more metals require considerably more sampling as the table on page 4 shows.

Obviously, sample variance is of great importance in determining sample size. Should future sampling indicate sample variances different from those used here, the sampling data should all be combined and new variances calculated. This may result in a lower estimate of adequate sample size and a cost saving.

APPENDIX 10[1]

NUMBER OF OBSERVATIONS FOR t-TEST OF DIFFERENCE BETWEEN TWO MEANS[2]

Reproduced from Table E.1 of Owen L. Davies, *The Design and Analysis of ...ustrial Experiments*, second ed., Oliver and Boyd, Edinburgh, 1956. By per-...ion of the author and publishers.

The entries in this table show the number of observations needed in a t-test ...he significance of the difference between two means in order to control the ...abilities of the errors of the first and second kinds at α and β, respectively. ...should be noted that the entries in the table show the number of observa-...s needed in *each* of two samples of equal size."

	Level of t-Test																				
	0.01					0.02					0.05					0.1					
Single-Sided Test	α = 0.005					α = 0.01					α = 0.025					α = 0.05					
Double-Sided Test	α = 0.01					α = 0.02					α = 0.05					α = 0.1					
β =	0.01	0.05	0.1	0.2	0.5	0.01	0.05	0.1	0.2	0.5	0.01	0.05	0.1	0.2	0.5	0.01	0.05	0.1	0.2	0.5	
0.05																					0.05
0.10																					0.10
0.15																					0.15
0.20																				137	0.20
0.25															124					88	0.25
0.30										123					87					61	0.30
0.35					110					90					64				102	45	0.35
0.40					85					70				100	50			108	78	35	0.40
0.45				118	68				101	55			105	79	39		108	86	62	28	0.45
0.50				96	55			106	82	45		100	86	64	32		88	70	51	23	0.50
0.55			101	79	46		106	88	68	38		87	71	53	27	112	73	58	42	19	0.55
0.60		101	85	67	39		90	74	58	32	101	74	60	45	23	89	61	49	36	16	0.60
0.65		87	73	57	34	101	77	64	49	27	87	63	51	39	20	76	52	42	30	14	0.65
0.70	100	75	63	50	29	90	68	55	43	24	76	55	44	34	17	66	45	36	26	12	0.70
0.75	88	66	55	44	26	79	58	48	38	21	67	48	39	29	15	57	40	32	23	11	0.75
0.80	77	58	49	39	23	70	51	43	33	19	59	42	34	26	14	50	35	28	21	10	0.80
0.85	69	51	43	35	21	62	46	38	30	17	52	37	31	23	12	45	31	25	18	9	0.85
Value of 0.90	62	46	39	31	19	55	41	34	27	15	47	34	27	21	11	40	28	22	16	8	0.90
0.95	55	42	35	28	17	50	37	31	24	14	42	30	25	19	10	36	25	20	15	7	0.95
$D = \frac{\delta}{\sigma}$ 1.00	50	38	32	26	15	45	33	28	22	13	38	27	23	17	9	33	23	18	14	7	1.00
1.1	42	32	27	22	13	38	28	23	19	11	32	23	19	14	8	27	19	15	12	6	1.1
1.2	36	27	23	18	11	32	24	20	16	9	27	20	16	12	7	23	16	13	10	5	1.2
1.3	31	23	20	16	10	28	21	17	14	8	23	17	14	11	6	20	14	11	9	5	1.3
1.4	27	20	17	14	9	24	18	15	12	8	20	15	12	10	6	17	12	10	8	4	1.4
1.5	24	18	15	13	8	21	16	14	11	7	18	13	11	9	5	15	11	9	7	4	1.5
1.6	21	16	14	11	7	19	14	12	10	6	16	12	10	8	5	14	10	8	6	4	1.6
1.7	19	15	13	10	7	17	13	11	9	6	14	11	9	7	4	12	9	7	6	3	1.7
1.8	17	13	11	10	6	15	12	10	8	5	13	10	8	6	4	11	8	7	6		1.8
1.9	16	12	11	9	6	14	11	9	8	5	12	9	7	6	4	10	7	6	5		1.9
2.0	14	11	10	8	6	13	10	9	7	5	11	8	7	6	4	9	7	6	4		2.0
2.1	13	10	9	8	5	12	9	8	7	5	10	8	6	5	3	8	6	5	4		2.1
2.2	12	10	8	7	5	11	9	7	6	4	9	7	6	5		8	6	5	4		2.2
2.3	11	9	8	7	5	10	8	7	6	4	9	7	6	5		7	6	5	4		2.3
2.4	11	9	8	6	5	10	8	7	6	4	8	6	5	4		7	5	4	4		2.4
2.5	10	8	7	6	4	9	7	6	5	4	8	6	6	4		6	5	4	3		2.5
3.0	8	6	6	5	4	7	6	6	4	3	6	5	4	4		5	4	3			3.0
3.5	6	5	5	4	3	6	5	4	4		5	4	4	3		4	3				3.5
4.0	6	5	4	4		5	4	4	3		4	4	3			4					4.0